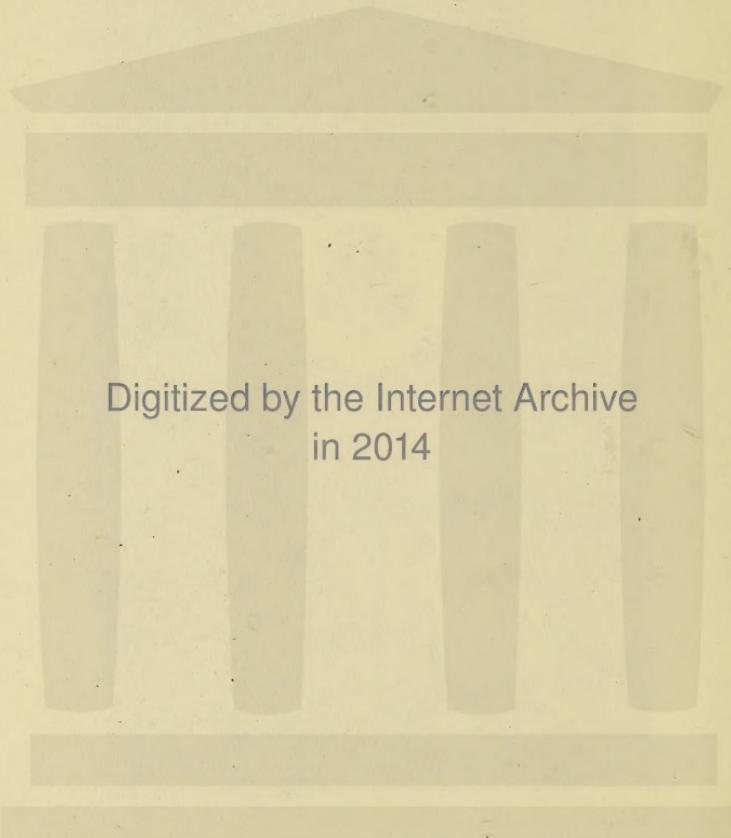


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ORIGINAL COMMUNICATIONS

EIGHTH INTERNATIONAL

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OF APPLIED CHEMISTRY**

Washington and New York

September 4 to 13, 1912

**APPENDIX
SECTION VIa TO SECTION XIb**



VOL. XXVI

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VOLUME XXVI.

APPENDIX—SECTION VIa TO SECTION XIb.

CONTENTS

Section VIa. Starch, Cellulose and Paper

| | PAGE |
|---|------|
| CROWN, HARRY A. (see PORST, CHRISTIAN, E. G.) | |
| GRUJIĆ, G. <i>Ueber Die Fettbestimmung Im Brot</i> | 1 |
| HERLES, FRANZ <i>Polarimetrische Stärkebestimmung in Kartoffeln</i> | 5 |
| PAROW, E. <i>Die Herstellung Des Dextrins Und Seine Verwendung</i> | 11 |
| PORST, CHRISTIAN E. G., AND CROWN, HARRY A. <i>A Polarimetric Method for the Determination of Starch in Paper</i> | 13 |
| STERLING, E. A. <i>The Development and Status of the Wood Preserving Industry in America</i> | 17 |
| WREDE, HANS <i>Combinierte Mineral-Stärkeleimung Für Druckpapier</i> | 31 |

Section VIb. Fermentation

| | |
|--|----|
| ALWOOD, WILLIAM B. <i>Sugar and Acid Content of American Native Grapes</i> | 33 |
| ALWOOD, WILLIAM B. <i>The Composition of Pure Wine from American Native Grapes</i> | 35 |
| CHAPMAN, A. CHASTON <i>The Application of the Mash-Filter to the Production of Infusion Beers</i> | 37 |
| FOTH, G. <i>Die Betriebsweise der Deutschen Brennereien Nach Aufhebung der Maischraumsteuer</i> | 47 |

| | PAGE |
|---|------|
| KALTENBACH, H. J. <i>The Laws of Man in Their Relation to the Manufacture and Sale of Products Resulting from the Natural Law of Fermentation.....</i> | 53 |
| KOENIG, A. G. <i>Modern Methods of Brewery Refrigeration.....</i> | 57 |
| NEUMANN, M. P. <i>Studien Über den Brotteig: Zähigkeitsmessungen.....</i> | 63 |
| ORTVED, NIELS C. <i>The Application of Taka-Koji in Distilleries.....</i> | 69 |
| RACH, CARL <i>The Qualitative Regulation of the Extract of Beer-Wort and Beer in Brewery Practice.....</i> | 77 |
| SCHLICHTING, EMIL <i>Relation of the Reducing Power to the Fermentative Capacity of Vari- ous Carbohydrates</i> | 83 |
| STRAUS, W. L. <i>The Growth and Development of the Bottling Beer Industry of the U. S.....</i> | 85 |

Section VII. Agricultural Chemistry

| | |
|---|-----|
| BLAIR, A. W. (see LIPMAN, J. G.) | |
| BREAZEALE, J. F. (see LECLERC, J. A.) | |
| BROWN, LUCIUS P. <i>The Phosphate Deposits of Continental North America</i> | 87 |
| HAIGH, L. D. <i>A Study of the Variations in Chemical Composition of the Timothy and Wheat Plants during Growth and Ripening.....</i> | 115 |
| JODIDI, S. L. <i>Behavior of Amino Acids in the Soil.....</i> | 119 |
| LECLERC, J. A. AND BREAZEALE, J. F. <i>The Effect of Lime upon the Alkali Tolerance of Wheat Seedlings....</i> | 135 |
| LECLERC, J. A. AND YODER, P. A. <i>Tri-Local Soil-Exchange Experiments with Wheat.....</i> | 137 |
| LIPMAN, J. G., BLAIR, A. W., OWEN, I. L. AND McLEAN, H. C. <i>Factors Relating to the Availability of Nitrogenous Plant-Foods....</i> | 151 |
| MCLEAN, H. C. (see LIPMAN, J. G.) | |
| MORGAN, L. E. <i>A Study of the Composition of Beef Fat as Influenced by Age and Condition of the Animal and Location in the Body.....</i> | 155 |

| | PAGE |
|--|------|
| MOULTON, C. ROBERT | |
| <i>A Study of the Cost of Maintenance and Growth and of the Changes in the Composition of the Mature Beef Animal during the Fattening Period</i> | 157 |
| OWEN, I. L. (see LIPMAN, J. G.) | |
| TASHIRO, SHIRO | |
| <i>New Method of Detecting Vitality of Seeds</i> | 163 |
| TRNKA, R. | |
| <i>L'Influence de L'Elektricité Statique sur le Développment la Récolte et la Composition de la Betterave A'Sucre</i> | 165 |
| YODER, P. A. (see LECLERC, J. A.) | |

Section VIIIa. Hygiene

| | |
|---|-----|
| ADAMS, GEORGE O. (see CLARK, H. W.) | |
| CHICK, HARRIETTE | |
| <i>The Factors Conditioning the Velocity of Disinfection</i> | 167 |
| CLARK, H. W. AND ADAMS, GEORGE O. | |
| <i>Studies of Fish Life and Water Pollution</i> | 199 |
| COPELAND, WILLIAM R. AND SOPER, GEORGE A. | |
| <i>Determination of Nitrates in Sea Water</i> | 211 |
| JENNINGS, C. A. | |
| <i>What Hypochlorite Sterilization of Water Supplies has Accom- plished in Several Cities</i> | 215 |
| KELLERMAN, KARL F. | |
| <i>The Rational use of Disinfectants and Algicides in Municipal Water Supplies</i> | 241 |
| LEWIS, W. LEE | |
| <i>The use of Hypochlorite in Checking a Mild Typhoid Epidemic at Evanston, Ill</i> | 247 |
| PARSONS, PAYN B. (see SOPER, GEORGE A.) | |
| PHELPS, EARLE B. | |
| <i>Bio-Chemistry of Sewage</i> | 251 |
| RIDEAL, S. | |
| <i>Suggested International Test for Disinfectants</i> | 261 |
| SHUTT, FRANK T. | |
| <i>The Water-Supply of Farm Homesteads in Canada</i> | 263 |

| SOPER, GEORGE A. | PAGE |
|--|------|
| <i>New Form of Apparatus for the Determination of Dissolved Oxygen in Water.....</i> | 265 |
| SOPER, GEORGE A. AND PARSONS, PAYN B. | PAGE |
| <i>A Practical Field Method for the Determination of Dissolved Oxygen in Water.....</i> | 267 |
| SOPER, GEORGE A. (see also COPELAND, WILLIAM R.) | |
| WHIPPLE, GEORGE C. | |
| <i>Sanitary Protection of the Water Supplies Taken from the Great Lakes.....</i> | 271 |
| WINSLOW, C.-E. A. | |
| <i>The Prevention of Industrial Poisonings.....</i> | 309 |
| Section VIIIb. Pharmaceutical Chemistry | |
| ARNY, H. V. | |
| <i>International Standards for Colored Fluids and a Suggested Plan for such Standardization.....</i> | 319 |
| BUCHKA, K. V. | |
| <i>Ueber den Methylalcohol.....</i> | 329 |
| FORRESTER, GEORGE P. (see MACEWAN, PETER) | |
| JEANCARD, PAUL AND SATIE, CONRAD | |
| <i>Contribution to the Unification of Methods of Analysis of Essential Oils.....</i> | 331 |
| PARRY, E. J. (see UMLEY, JOHN C.) | |
| SATIE, CONRAD (see JEANCARD, PAUL) | |
| UMLEY, JOHN C. AND PARRY, E. J. | |
| <i>Unification of Processes for Commercial Analysis and Valuation of Essential Oils.....</i> | 341 |
| MACEWAN, PETER AND FORRESTER, GEORGE P. | |
| <i>International Commission on Variations in the Activity of Certain Toxic Drugs. Preliminary Report by the Secretaries.....</i> | 349 |
| Section VIIIc. Bromatology | |
| BITTING, K. G. | |
| <i>Methods for Determining Antiseptic Properties.....</i> | 353 |
| BUCHKA, K. VON | |
| <i>Fortbildungskurse für Nahrungsmittelchemiker.....</i> | 355 |
| DUNBAR, P. B. | |
| <i>The Determination of Tartaric Acid.....</i> | 361 |

| | PAGE |
|--|------|
| DUNBAR, P. B. <i>The Determination of Malic and Tartaric Acids in the Same Solution.....</i> | 375 |
| GOULD, RALPH A. <i>The Specific Gravity of Citrus Fruit as a Factor in the Separation of Frozen Fruit.....</i> | 387 |
| GOULD, R. A. <i>The Gases Evolved from Roasted Coffee, Their Composition and Origin.....</i> | 389 |
| HEPBURN, J. S. (see PENNINGTON, M. E.) | |
| MCGILL, A. <i>National Control of Food in Canada.....</i> | 391 |
| NICOLIC, E. <i>Cultura ed Industria Dell'Amarasco in Dalmazia.....</i> | 395 |
| PENNINGTON, M. E. AND HEPBURN, J. S. <i>Studies on Chicken Fat.....</i> | 401 |
| PENNINGTON, M. E. AND ROBERTSON, H. C., JR. <i>On a Study of the Enzymes of the Egg of the Common Fowl.....</i> | 405 |
| ROBERTSON, H. C., JR. (see PENNINGTON, M. E.) | |
| SMITH, CLAUDE R. <i>The Determination of Arsenic.....</i> | 407 |
| WINTON, A. L. <i>The Chloral Hydrate Test for Charlock.....</i> | 409 |
| Section VIIId. Biochemistry including Pharmacology | |
| AGULHON, H. (see BERTRAND, GABRIEL) | |
| BERTRAND, GABRIEL AND AGULHON, H. <i>Sur la Présence Normale du Bore Chez Les Animaux.....</i> | 413 |
| WOLEF, JULES <i>Sur une Nouvelle Fonction du Catalyseur Dit "Peroxydase" et sur la Transformation Biochimique de L'Orcine en Orcéine.....</i> | 417 |
| Section IX. Photochemistry | |
| BAEKELAND, L. H. <i>The Permanency of Gold-Toned Silver Prints.....</i> | 421 |
| FERY, M. CH. <i>La Spectographie et ses Applications.....</i> | 423 |

| IVES, HERBERT E. | PAGE |
|---|------|
| <i>Recent Advances in our Knowledge of Cold Light</i> | 433 |
| IVES, HERBERT E. | 439 |
| <i>Recent Progress in Photometry</i> | 439 |
| IVES, HERBERT E. | 447 |
| <i>The Present condition of Color Photography</i> | 447 |

Section Xa. Electrochemistry

| | |
|---|-----|
| ASTON, JAMES AND BURGESS, CHARLES F. | |
| <i>The Rate of Rusting of Iron and Steel</i> | 453 |
| ASTON, JAMES (see also BURGESS, CHARLES F.) | |
| BRADLEY, LINN | |
| <i>Electrical Precipitation of Dust and Fumes</i> | 471 |
| BURGESS, CHARLES F. AND ASTON, JAMES | |
| <i>Influence of Various Elements on the Corroductility of Iron</i> | 479 |
| BURGESS, CHARLES F. (see also ASTON, JAMES) | |
| CLEMENT, J. K. AND WALKER, L. V. | |
| <i>An Electrolytic Method for the Prevention of the Corrosion of Iron and Steel</i> | 491 |
| DANIELS, F. (see RICHARDS, THEODORE W.) | |
| FINK, COLIN G. | |
| <i>Applications of Ductile Tungsten</i> | 503 |
| HAMBUECHEN, CARL AND RUHOFF, O. E. | |
| <i>Some Physical and Chemical Data on Dry Cells and Dry Cell Material</i> | 509 |
| KOWALKE, O. K. | |
| <i>Some Observations on Base Metal Thermocouples</i> | 515 |
| LYON, D. A. | |
| <i>Reduction of Iron Ores in the Electric Furnace</i> | 519 |
| PALMAER, W. | |
| <i>On the Method of Producing Bicalcic Phosphate with the Help of Electrolytically Produced Acid and Alkali</i> | 541 |
| RICHARDS, THEODORE W. AND DANIELS, F. | |
| <i>The Electrochemical Behavior of very Concentrated Thallium Amalgams</i> | 553 |
| RUHOFF, O. E. (see HAMBUECHEN, CARL) | |
| SCHULTE, WALTER B. | |
| <i>The influence of Cinders on the Corrosion of Iron Imbedded in Clay</i> | 555 |
| WALKER, L. V. (see CLEMENT, J. K.) | |

Section Xb. Physical Chemistry

| | PAGE |
|---|------|
| ACREE, S. F. (see ROBERTSON, H. C.) | 561 |
| BATES, STUART J. (see WASHBURN, EDWARD W.) | 561 |
| BUCKNER, G. D. AND HULETT, G. A. | |
| <i>Studies on the Silver Coulometer</i> | 565 |
| CADY, W. G. | |
| <i>The Vaporization of Metallic Cathodes in the Glow Discharge</i> | 567 |
| GETMAN, FREDERICK H. | |
| <i>Absorption Spectra of Solutions of Some Periodides</i> | 569 |
| HULETT, G. A. (see BUCKNER, G. D.) | |
| HULETT, G. A. (see LAIRD, J. S.) | |
| JÄNECKE, ERNST | |
| <i>Ueber Reziproke Salzpaare und Doppeltternäre Salzmischungen</i> | 571 |
| JUDD, ROY C. (see WALTON, JAMES H. JR.) | |
| LAIRD, J. S. AND HULETT, G. A. | |
| <i>The Inclusions in Electrolytic Silver and Their Effect on the Electrochemical Equivalent of Silver</i> | 599 |
| LOEB, MORRIS | |
| <i>Studies in the Speed of Reductions</i> | 601 |
| LOWRY, T. MARTIN | |
| <i>Standard Wave-lengths for use in Optical Measurements</i> | 605 |
| MCCOY, HERBERT N. AND VIOL, CHARLES H. | |
| <i>The Chemical Properties and Relative Activities of the Radio-products of Thorium</i> | 607 |
| ROBERTSON, H. C. AND ACREE, S. F. | |
| <i>On the Conductivity and Ionization of Sodium Ethylate, Potassium Ethylate, Lithium Ethylate, Sodium Phenolate, Potassium Phenolate, Lithium Phenolate, Sodium Phenylthiourazole, Sodium Iodide, Sodium Bromide, and of Mixtures of these electrolytes, in absolute ethyl Alcohol at 0°, 25°, and 35°</i> | 609 |
| ROTHMUND, VICTOR | |
| <i>Ueber die Reaktion Zwischen Ozon und Wasserstoffperoxyd</i> | 611 |
| STRONG, W. W. | |
| <i>The Electrical Precipitation of Carbon Smoke</i> | 617 |
| VIOL, CHARLES H. (see MCCOY, HERBERT N.) | |
| WALTON, JAMES H. JR., AND JUDD, ROY C. | |
| <i>The Preservation of Hydrogen Peroxide</i> | 621 |

| | PAGE |
|---|------|
| WASHBURN, EDWARD W. AND BATES, STUART J. <i>The Iodine Coulometer and the Value of the Faraday</i> | 623 |
| WEINTRAUB, E. <i>Boron</i> | 627 |
| Section XIa. Law and Legislation Affecting Chemical Industry | |
| DAVIS, C. A. AND THOMPSON, J. W. <i>The Conservation of the Atmosphere: The Use and Misuse of the Air—Legal Phases of Right in Air</i> | 649 |
| EPHRAIM, J. (see ISAY, H.) | |
| ISAY, H. AND EPHRAIM, J. <i>Patentschutz für Pharmazeutische Produkte</i> | 653 |
| KLOEPPEL, E. <i>Der Akzessorische Charakter des Markenschutzes</i> | 657 |
| MEINHARDT W., IST. <i>Ausübungs-Und Lizenzzwang</i> | 663 |
| MINTZ, M. <i>Einheitlicher Patent,—Muster-Und Marken-Schutz</i> | 671 |
| OSTERRIETH, A. <i>Die Lage des Gewerblichen Rechtsschutzes in Deutschland</i> | 679 |
| THOMPSON, J. W. (see DAVIS, C. A.) | |
| WASSERMANN, M. <i>Das Prioritätsrecht der Pariser Konvention</i> | 689 |
| Section XIb. Political Economy and Conservation of Natural Resources | |
| ARNOLD, RALPH AND CLAPP, FREDERICK G. <i>The Movement for Conservation of Natural Gas in the United States</i> | 695 |
| CAMERON, FRANK K. <i>What the United States is doing toward the Conservation and Improvement of Soil Fertility</i> | 699 |
| CLAPP, FREDERICK G. (see ARNOLD, RALPH) | |
| DAVIS, CHARLES A. <i>Peat as Fuel</i> | 707 |
| HESS, RALPH HENRY <i>Some Economic Aspects of Conservation</i> | 711 |

| | PAGE |
|--|------|
| HOLMES, J. A. <i>The National Phases of the Mining Industry</i> | 733 |
| LEIGHTON, M. O. <i>Hydrometric Work of the United States Government</i> | 751 |
| PLUMMER, FRED G. <i>Prevention and Control of Forest Fires</i> | 753 |
| PRICE, OVERTON W. <i>The Conservation of Forests by Private Landholders in the United States</i> | 763 |
| SMITH, GEORGE OTIS <i>A Business Policy for a National Domain</i> | 769 |
| SPRING, SAMUEL N. <i>State Work in Forest Conservation</i> | 777 |
| TAYLOR, SAMUEL A. <i>Conservation as Applied to Bituminous Coal Industry</i> | 779 |
| WILSON, HERBERT M. <i>Fire Losses in the United States and Their Prevention</i> | 787 |
| SPECIAL PAPER <i>The Activities of England, Wales and the Dominion of Canada in Behalf of the Conservation of National Resources</i> | 791 |
| SPECIAL PAPER <i>Regulations Established by the Government of Chile in Order to Promote the Practical Conservation of the Natural Resources Offered by the Waters (of the Country), to Obtain Maximum Water Power in Order to Secure to the Community and to the State the Maximum of Advantages. Certain Facts Illustrating these Provisions</i> | 821 |

UEBER DIE FETTBESTIMMUNG IM BROT

G. GRUJIC

*Mitteilung aus der Versuchsanstalt für Getreideverarbeitung,
Berlin, Germany*

Dem Fett kommt als Bestandteil des Mehles nur eine untergeordnete Bedeutung zu. Auch für die Mehlbeurteilung vom müllereitechnischen Standpunkt hat seine Bestimmung an Interesse verloren, nachdem der Vorschlag die Mehle nach dem Fettgehalt einzuordnen, auf allgemeinen Widerstand gestossen ist. Beachtenswerter ist es vielleicht vom Gesichtspunkt der Mehllagerung, bei der es infolge seiner leichten Zersetzlichkeit von Einfluss sein kann.

Andererseits wird die Ermittlung des Fettgehaltes in Diabetikermehlen und besonders in Gebäcken, wenn es sich darum handelt Milch und Butter enthaltende Gebäcke zu beurteilen, Beachtung verdienen.

Die Fettbestimmung ist in ihrem grundsätzlichen Verlauf bekanntlich sehr einfach. Eine bestimmte Menge des zu untersuchenden Stoffes wird mit dem Fettlösungsmittel vollständig erschöpft und das in das Fettlösungsmittel übergegangene Fett gewogen. Diese einfache Arbeitsweise versagt nun aber beim Brot, sei es Roggen- oder Weizenbrot- Schwarz- oder Weissgebäck, *vollständig*. Diese Beobachtung wurde von M. Weibull bereits im Jahre 1892 gemacht und später von E. Polenske bestätigt.¹ Sie scheint jedoch in der Laboratoriumspraxis wenig Beachtung gefunden zu haben.

Auf Veranlassung des Herrn M. P. Neumann, Versuchsanstalt für Getreideverarbeitung—Berlin habe ich diese Frage mit H. Kalning erneut in Angriff genommen, umso mehr, als die von den genannten Autoren empfohlenen Methoden recht unständlich und zum Teil ungenau zu sein schienen.

¹ Zeitschrift für angewandte Chemie 1892 und Arb. Kriser Gesundheits—Amt. 1893.

Unsere Fettbestimmungsversuche bestätigten die Tatsache, dass es weder durch Abänderung der Vortrocknung noch durch die feinste Vermahlung, die Ausbeute an Fett zu erhöhen, gelingt. Durch Extraktion der ganz frischen Brotkrume erhält man nahezu den ganzen Fettgehalt des Brotes, d. h. die Menge Fett, die in der Trockensubstanz des verwendeten Mehle gefunden wurde. Es ergab sich jedoch, dass bei Roggenbrot, das mit Sauerteig hergestellt ist, diese Arbeitsweise nicht brauchbar ist, dagegen kann man sich bei Weizengebäck, das mit Hefe bereitet wurde, wenn es sich nur um eine Orientierung des Fettgehaltes handelt, mit der Extraktion der feuchten Krume begnügen.

Als Ursache der geringen Fettzahlen bei Extraktion älterer Backware erkannten wir den Zustand des Altbackenseins, bei dem durch den Uebergang der Stärke in den amorphen Zustand eine solche Festlegung des Fettes eintritt, dass es sich der Einwirkung der Lösungsmittel entzieht.

Es musste daher eine andere Methode zur Fettbestimmung im Brot gesucht werden, und wir haben zunächst die bereits aus der Literatur bekannten Arbeitsweisen geprüft. Der Grundgedanke aller dieser Methoden ist der, die Stärke durch Hydrolyse aufzuspalten, um das Fett frei zu legen und der Ermittlung zugänglich zu machen.

Die besten Fettwerte gab uns die Methode nach Polenske; nach Berntrop und vor allem nach Weibull werden zu hohe Zahlen gefunden. Die Fettbestimmung nach Polenske erschien uns jedoch insofern einer Abänderung zugänglich, als die Dauer der Durchführung eine recht langwierige ist und das Arbeiten mit Chloroform Schwierigkeiten verursacht.

Der Gang der Fettbestimmung im Brot ist nach unserer Arbeitsweise, die sich an Polenske's Methode stützt, folgender:

5 g der Brotkrume, die man in feuchtem Zustande zerkrümeln oder in vorgetrocknetem Zustande mahlen kann, werden in einem 200 ccm fassenden, mit Steigrohr versehenen Kölbchen mit 50 ccm Wasser und 2 ccm 25% Salzsäure ($D = 1,125$) $1\frac{1}{2}$ Stunden lang in siedendem Wasserbad der Hydrolyse unterworfen. Nach dem Erkalten fügt man 1 ccm einer verdünnten Metylorangelösung (0.04%) hinzu, neutralisiert mit konzen-

trierter Natronlauge und säuert mit einem Tropfen verdünnter Salzsäure an. Es wird durch ein kleines Faltenfilter filtriert, der Rückstand mit heissem Wasser ausgewaschen und mit dem Filter (unter Ausbreiten auf einem Uhrglase) zwei Stunden bei 105° getrocknet. Man extrahiert nun den in eine Soxhlet'sche Fetthülse übergeführten Rückstand nebst Filter 6 Stunden mit Aether.

Es wurden folgende Resultate mit dieser Arbeitsweise erzielt:

| | | | Fett in der |
|------|---|--------|-----------------------------|
| | | | Wasser Fett Trockensubstanz |
| I. | Roggenbrot (vorgetrocknet) | | |
| " | " | 5,19% | 1,33% 1,40% |
| " | " | 5,19% | 1,28% 1,35% |
| " | (feucht) | 5,19% | 1,34% 1,41% |
| " | (vorgetrocknet) | 44,8% | 0,69% 1,25% |
| " | " | 8,23% | 1,31% 1,43% |
| " | " | 8,23% | 1,27% 1,38% |
| " | " | 8,23% | 1,26% 1,37% |
| " | " | 8,23% | 1,14% 1,24% |
| " | " | 1,42% | 1,33% 1,35% |
| " | " | 1,42% | 1,35% 1,37% |
| II. | Weizenbrot (vorgetrocknet) | | |
| " | " | 9,39% | 1,53% 1,68% |
| " | " | 9,39% | 1,52% 1,67% |
| " | " | 9,39% | 1,33% 1,47% |
| " | (feucht) | 9,39% | 1,45% 1,6% |
| " | (feucht) | 43,62% | 0,95% 1,69% |
| " | (feucht) | 43,62% | 0,93% 1,65% |
| III. | Weizengebäck mit Magermilch (vorgetrocknet) | | |
| " | " | 1,05% | 1,2% 1,21% |
| " | " | 1,05% | 1,18% 1,17% |
| " | " | 1,05% | 1,18% 1,19% |
| " | " | 8,28% | 1,54% 1,68% |
| " | " | 8,28% | 1,56% 1,7% |
| IV. | Weizengebäck mit Vollmilch (vorgetrocknet) | | |
| " | " | 1,27% | 2,32% 2,35% |
| " | " | 1,27% | 2,40% 2,43% |
| " | " | 1,27% | 2,31% 2,34% |

In der Trocken-
Mehles
1,27% Fett

In der Trocken-
substanz des
Mehles
1,54% Fett

Fett des Mehles
1,74%

Berechnet
1,39% Fett (i.
Trockensubst.)

Berechnet

1,88% Fett

Berechnet

2,5% Fett

Die auf diese Weise gefundenen Fettzahlen stimmen mit den aus den Mehlen berechneten genügend überein so dass diese bequem durchzuführende Arbeitsweise m. E. noch den Vorzug verdient.

POLARIMETRISCHE STÄRKEBESTIMMUNG IN KARTOFFELN

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Der Stärkegehalt der Kartoffeln pflegt in der Praxis hauptsächlich auf Grund deren specif. Gewichtes bestimmt zu werden. Die Mängel der auf diesem Prinzipie basirenden Methoden sind allgemein bekannt.

Für genauere Untersuchungen muss deshalb zu den chemischen Methoden gegriffen werden.

Von diesen sind einige auf der Ueberführung der Stärke in Stärkezucker begründet, welcher sodann nach bekanntem Verfahren von Alihn, Kruis u. a. mittels der Fehling's cher Lösung bestimmt wird, oder es wird die Stärke durch verschiedene Agentien in Lösung überführt und polarimetrisch bestimmt.

Die, auf der Ueberführung der Stärke in Stärkezucker und dessen Bestimmung durch die Reduktion der Fehling'schen Lösung basirenden Verfahren sind ziemlich mühsam und erfordern viel Zeit zu ihrer Ausführung, wogegen die polarimetrischen Verfahren sich leichter und schneller ausführen lassen.

Von diesen ist das Vefahren nach Baudry bekannt, welches auf der Löslichkeit der Stärke in heißer Salicylsäure begründet ist.

Effront benützt zur Auflösung der Stärke Salzsäure und benützt das Verfahren hauptsächlich zur Stärkebestimmung in Getreidearten.

Neulich hat auf diesen Prinzipie C. J. Lintner mit Belschner ein Verfahren zur Stärkebestimmung in der Gerste ausgearbeitet.

Wengelin bringt zu diesem Zwecke die Stärke mittels Schwefelsäure ($\text{sp.G.} = 1.70$) in Lösung.

Fr. Schubert überführt die Stärke durch 5-stündigtes Kochen im Wasserbade mittels einer besonderen Flüssigkeit (sog. Abbaulösung, enthaltend 10% NaCl und 1% HCl) in Stärkezucker, und polarisiert die Lösung.

Da ich seiner Zeit eine grössere Anzahl von Stärkebestimmungen in Kartoffeln durchzuführen hatte und auf Grund von Vergleichsversuchen erkannt habe, dass der aus dem specif. Gewichte ermittelte Stärkegehalt öfters bis um mehrere Prozente differierte, habe ich mich im Jahre 1904 für die Polarisationsmethode und zwar auf Grund des Effront'schen Prinzipes entschlossen.

Zu diesem Zwecke bereitete ich aus der Durchschnittsprobe von Kartoffeln mittels meines Apparates zur Gewinnung des feinsten Rübenbreies für momentane kalte Wasser digestion (Herles'sche Presse) einen sehr feinen Brei.

Das Prinzip dieses Apparates besteht darin, dass in einem engen Presszylinder (Dm. 18 mm), welcher mit gelochtem und mit feinen Kupfersieb überdeckten Boden versehen ist, ein dicht anliegender Presskolben bewegt wird, mittels welchen Pflanzenteile (wie Rübe, Kartoffeln, etc.), durch das feine Sieb gepresst und in feinsten Brei verwandelt werden.

Auf diese Weise bereiteter hochfeiner Brei ermöglicht nämlich eine vollständige und leichte Auflösung der Stärke in Salzsäure ohne jedwedes weitere Zerreiben in der Reibschale oder dgl. un zwar durch blosses Vermischen des Breies mit verdünnter Salzsäure und zeitweises Umrühren.

Zur Bereitung des feinsten Kartoffelbreies mit der Herles'schen Presse entnimmt man entweder einen Durchschnittsmuster vom auf gewöhnliche Art gewonnenen Brei (mit Reibeisen, oder durch eine Hackmaschine, z. B. der amerik. Marke "Keystone") oder es werden direkt Kartoffelteile (z. B. Viertel) im genannten Apparate in feinsten Brei verwandelt.

Es wurde ferner nötig das Drehungsvermögen der reinen Kartoffelstärke in verdünnter Salzsäure und bei 20°C zu ermitteln.

Zu diesem Zwecke wurden aus mehreren Erzeugungsstellen Muster von reinster Ia Kartoffelstärke verschafft und dieselben im Laboratorium weiterer Reinigung unterzogen. (Mehrmaliges Aufrühren mit destil. Wasser und Absetzenlassen nur der schwersten Stärkekörner, Austrocknen über Schwefelsäure).

Zur Polarisation wurde von jedem, fein zerriebenen Muster je 2, 4, 6, 8 u. 10 g gereinigter Stärke abgewogen, in ein 100 cc

Kölbchen gebracht, 25 cc Wasser zugesetzt, zur gleichmässigen Suspendirung der Stärke umgerührt, nachher unter fortwährendem Umrühren 25 cc rauchender Salzsäure (sp. G. = 1.188) zugefügt und unter zeitweisem Umrühren ca 1 Stunde stehen gelassen. Dieses Konzentrationsverhältnis der Salzsäure ist erforderlich einzuhalten, denn verdünntere Säure löst die Stärke nicht vollständig auf, eine stärkere Säure könnte dagegen zerstörend wirken. Nachher wurde mit Wasser nachgefüllt und bei 20°C zur Marke gebracht, filtriert und im kontrollierten Wentzke-Soleil'schen Halbschattenapparate von der Firma J. J. Fric, Kgl. Weinberge, Prag, polarisiert. Man kann auch ohne merklichen Fehler zu begehen bei von 20°C etwas abweichender Temperatur auffüllen und polarisieren, nur muss selbstverständlich möglichst bei derselben Temperatur aufgefüllt werden, bei welcher die Polarisation stattfindet.

Die gefundene Polarisation wurde auf reine wasserund aschenfreie Stärke umgerechnet und diejenige Menge solcher reinen Stärke ermittelt, welche der Polarisation von 100% entspricht. Aus den Zahlen, welche durch Abwiegen verschiedener Mengen Stärke einer und derselben Provenienz erhalten wurden und welche unbedeutend differierten, wurde die Durchschnittszahl für die betreffende Stärkemarken berechnet.

Hierbei wurde gefunden, dass zur Erlangung einer Polarisation von 100% wurde erforderlich an reiner wasser- und aschenfreien Stärke abzuwiegen bei der Kartoffelstärke

| | | |
|-----|------|----------|
| Nr. | I. | 8.839 g, |
| | II. | 8.754 g, |
| | III. | 8.921 g, |
| | IV. | 8.796 g, |
| | V. | 8.796 g, |

im Durchschnitte: 8.821 g.

Diese Durchschnittszahl entspricht demnach der s. g. Normalmenge für die Polarisation, d. h. jener Menge, welche, auf 100 cc abzuwiegen wäre um bei der Polarisation im Wentzke-Soleilschen Apparate direkt Prozente Stärke ablesen zu können. Diese, für die Salzsäure bei angegebener Verdünnung ermittelte

Zahl entspricht einem spezifischen Drehungsvermögen von 196.25°

Bisher wurden für das Drehungsvermögen der Stärke folgende Zahlen ermittelt:

Baudry (für heiße Salicylsäure) (α)²⁰ D = +200.0°

(entsprechend dem Normalgewichte 8.65 g)

Effront (für Salzsäure) (α)²⁰ D = +193.0°

(entsprechend dem Normalgewichte 8.97)

Wengelin (für verdünnte H₂ SO₄, sp. G. 1.70)²⁰ (α)²⁰ D = +191.6°

(entsprechend dem Normalgewichte 9.03)

Lintner (für Salzsäure) (α)²⁰ D = +200.1°

(entsprechend dem Normalgewichte 8.65)

Herles (für verdünnte Salzsäure) (α)²⁰ D = +196.25°

(entsprechend dem Normalgewichte 8.82)

Unsere Zahl nähert sich sehr dem Durchschnitte der Zahlen von

$$\text{Effront und Lintner: } \frac{193.0 + 200.1}{2} = +196.55^\circ \text{ resp. } \frac{8.65 - 8.97}{2}$$

$$= 8.81 \text{ g.}$$

Nach dem beschriebenen Verfahren lässt sich der Stärkegehalt in stärkehältigen pulverigen Stoffen, z. B. in verkäuflichen Stärkesorten, Mehlen, etc. leicht bestimmen. Die Reisund Weizenstärke, sowie Mehle lieferten nach dieser Metode mit der Reduktionsmethode übereinstimmende Resultate.

Bei Untersuchung von Mehlen und feingeschrotteten Getreidearten empfiehlt es sich mit Phosphorwolframsäurelösung zu klären. Zu diesem Zwecke wird eine 0.5% Lösung dieser Säure bereitet, mit welcher zu 100 cc anstatt mit blossem Wasser aufgefüllt wird. Bei der Stärkebestimmung in Kartoffeln nach diesem Verfahren muss auch die Menge des Markes, d.h. des in Salzsäure unlöslichen Anteiles berücksichtigt werden. Ich habe im Jahre 1906 bei 144 verschiedenen Kartoffelsorten diesen unlöslichen Rückstand bestimmt und Zahlen gefunden die zwischen 4.32 bis 6.87% variierten. Der Durchschnitt von allen diesen Bestimmungen war 5.41%. Dieses Mark nahm bei einem specif. Gewicht 1.35 einen Raum von $\frac{5.41}{1.35} = 4.0$ cc ein. Für das normale Gewicht = 8.82 g Brei entspricht dies 0.35 cc. Beim Arbeiten mit 100 cc Körbchen muss man demnach zu 100.35 cc auffüllen.

Bei der Stärkebestimmung in Kartoffeln wird demnach folgends verfahren:

Die normale Menge 8.82 g (für Mohr'sche cc) resp. 8.80 g (für metrische cc) gründlich durchgemischten feinsten Kartoffelbreies wird mit Hilfe von 25 cc Wasser in ein 100 cc Kölbchen gebracht, durchgerührt und sucseste unter stetem Umrühren um die Entstehung der verkleisterten Klumpen zu verhindern, 25 cc rauchender Salzsäure (sp.G. = 1.188) zugesetzt. Diese Mischung wird anfangs dicker infolge Kleisterbildung, verflüssigt sich aber bald. Nach ungefähr einer Stunde bei zeitweisem Umrühren wird mit Wasser zu 100.35 cc aufgefüllt, durchgeschüttelt, filtriert und polarisiert. Die abgelesenen Grade sind direkt Prozente der Stärke.

Für schnelles Arbeiten bei Massenuntersuchungen empfehle ich folgende, der kalten Wasserdigestion des Rübenbreies in Gefäßen (ohne Messkölbchen) analogische Modifikation.

Man wiegt 9.55 g (für die Mohr'schen cc) resp. 9.53 g (für die metrischen cc) gut durchgemischten, feinsten Kartoffelbreies ab, bringt ihn in ein Becherglas, spült das Wägeschälchen mit 25 cc Wasser und trocknet dasselbe mit ein Stückchen Flittrirpapier, welches in den Becher geworfen wird, ab, setzt unter stetem Umrühren (mit einem Stäbchen) 25 cc rauchender Salzsäure (sp.G. = 1.188) zu, lässt unter zeitweisem Umrühren ungefähr 1 Stunde stehen, fügt weitere 50 cc Wasser zu, schüttelt durch, filtriert und polarisiert. Die gefundenen Grade am polarimeter Wentzke-Soleil entsprechen den Stärkeprozenten in Kartoffeln.

Anstatt mit 50 cc Wasser, kann man auch 50 cc 0.5%-iger Phosphorwolphram säurelösung zusetzen; bei meinen bisherigen Versuchen erwies sich jedoch diese Klärung als entbehrlich.

Das abzuwiegende Quantum 9.55 g wurde auf Grund folgender Erwägung ermittelt: Das Normalgewicht für 100 cc = 8.82 g Brei. Der Kartoffelbrei enthält durchschnittlich 5.41% in Salzsäure unlöslichen Rückstand, somit in 8.82 g Brei 0.47 g. In die Lösung gehen demnach 8.82 g - 0.47 g = 8.35 g Kartoffelsubstanz über. Bei einem durchschnittlichen Stärkegehalte von 20%, würde somit eine Lösung vom specif. Gewichte ca 1.09 entstehen, welche ein Volum von $\frac{8.35}{1.09} = 7.66$ cc einnehmen

würde. Zur Gewinnung von 100 cc Polarisationslösung muss man demnach $100 - 7.66 = 92.34$ cc Wasser mit Salzsäure zusetzen. Werden jedoch 100 cc Wasser mit Salzsäure verwendet, muss man dementsprechend mehr Kartoffelbrei abwiegen, laut Proportion: $8.82:92.34 = \times : 100$ wobei $\times = \frac{8.82 \times 100}{92.34} =$

9.55 g.

Werden in den untersuchten Kartoffeln Zucker und andere polarisierende Nichtstärkestoffe, welche die polarimetrische Stärkebestimmung beeinflussen könnten, vermutet, kann man sich hievon auf folgende Weise überzeugen.

Man wiegt die Normalmenge feinsten Brei ab, bringt ihn mit Wasser in ein 100 cc Kölbchen, füllt mit blossem Wasser zu 100.35 cc auf, schüttelt gut durch und filtriert. Vom Filtrate werden 50 cc in ein anderes 100 cc Kölbchen gebracht, 25 cc rauchender Salzsäure zugesetzt und mit Wasser zu 100 cc aufgefüllt, durchgeschüttelt, filtriert und polarisiert. Man kann auch analog, ohne Kölbchen, im Becher, wie vorher beschrieben, arbeiten. Das verdoppelte Ergebnis wird im Falle einer Rechtsdrehung vom Stärkegehalte abgezogen, bei einer Linksdrehung hingegen zugerechnet.

(Auszug)

DIE HERSTELLUNG DES DEXTRINS UND SEINE VERWENDUNG

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Die erste Darstellung von Dextrin (Röstgummi) geschah im Jahre 1804 durch Bouillon Lagrange durch Einwirkung hoher Temperaturen auf Stärkemehl. Im Jahre 1811 veröffentlichte Vaucouelin diese Art der Herstellung von Dextrin und im selben Jahre stellte Kirchhoff, der Erfinder des Stärkezuckers, ein Dextrin durch Einwirkung von verdünnter Schwefelsäure auf Stärke her.

In chemischer Beziehung ist die Dextrinbildung als eine Atomumlagerung des Stärkemoloküls aufzufassen, bei welcher die Struktur des Stärkekornes nicht verändert wird, wohl aber eine wesentliche Veränderung der Eigenschaften der Stärke stattfindet. Die in Wasser unlösliche Stärke wird löslich, bildet mit Wasser eine fade schmeckende, klebrige Beschaffenheit besitzende Lösung, welche das prolavisierte Licht nach rechts ablenkt, Jodlösung blau-violett bis rot färbt, auf Alkoholzusatz weisse Flocken (Dextrin) ausscheidet und durch Hefe (Brauerei-, Brennerei-, Weinhefe) nicht, wohl aber durch Loggos- und Pombehefe vergoren wird. Das Dextrin des Handels besteht neben Dextrin aus ca. 10-12% Wasser, 0,3% Asche, 5% Dextrose und Säure, welche 3 ccm. Normalnatronlauge auf 100 g Dextrin entspricht. Es werden drei Arten der Herstellung von Dextrin unterschieden, das Rösten der Stärke ohne und mit Säurezusatz, die enzymatische Einwirkung auf Stärke und das Kochen der Stärke mit Säure. Die erstere hat für die Industrie den grössten Wert, die zweite kommt für die Praxis nicht in Frage und die dritte hat nur eine untergeordnete Bedeutung. Die Dextrinherstellung geschieht hauptsächlich in der Weise,

das Stärkemehl in geeigneten Apparaten ohne oder mit geringen Mengen Säure (Salzsäure, salpetersäure) gemischt, evtl. scharf getrocknet und in gemahlenem Zustande dem Röstapparat (Uhland, Lehmann, Wulkan) zugeführt wird und hier bei Temperaturen von über 100–250°C. (Röstgummi) resp. 100–150°C. (Säuredextrin) 1–2 Stunden erhitzt wird. Das fertige Dextrin wird dann in geeigneten Apparaten (Uhland, Göhring und Hebenstreit) gekühlt, befeuchtet, gemahlen und gesichtet. Von den verschiedenen Dextrinverfahren werden diejenigen von Blumenthal, Fielding, Göhring und Hebenstret, Harvey (Anwendung von Elektrizität), Pieper (Anwendung von Ozon) Uhland und Wulkan und Neumann besprochen. Kristallgummi wird durch Auflösen von gelbem Dextrin in heissem Wasser, entfärbten der Lösung durch Knochenkohle, Filtration und Eindampfung der Lösung und Zerkleinerung der bis zur Trockenheit eingedampften Masse gewonnen.

Die Verwendung des Dextrins geschieht hauptsächlich in der Textilindustrie, Papierindustrie, Kristall—Gummierfabrikation, Zündholzfabrikation und Fabrikation der Kaltleime (Russischer Leim, Universalleim).

Die Produktion an Dextrin in Deutschland beträgt jährlich ca. 300000 Dz., die Ausfuhr von Dextrin aus Deutschland jährlich ca. 80–90000 Dz. Die Hauptabsatzgebiete für Dextrin sind Grossbritannien und Amerika.

A POLARIMETRIC METHOD FOR THE DETERMINATION OF STARCH IN PAPER

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Chemical laboratories have quite often been confronted by the problem of determining quantitatively the starch in paper. Nearly all paper mills use a certain amount of starch, and it is of importance to the manufacturer of starch as well as to the manufacturer of paper to know exactly how much of the starch is retained by the paper.

Several methods had been suggested and we have tried, in the last couple of years, some of these, but we have been unable to get, by these methods, any results which we could consider fully satisfactory. Furthermore, the methods were, with the exception of the very inaccurate colorimetric method, very complex, requiring many manipulations, as for instance Diastase Method, recommended by Schumann (*Papier Zeitung* 1887), Märckers Diastase Method or Reinke's Autoclave Method.

Trying to work out a simple, accurate and quick method, we decided to investigate the possibilities of determining polarimetrically the starch in paper. In another paper, ("Research on Lintner's Polarimetric Method for the Determination of Starch") we have determined the specific rotatory power of corn starch in solutions of concentration of 5 gms. 200 c.c. In paper there is present only a small percentage of starch, and in order to get a solution of the same concentration, it would be necessary to work with too large an amount of paper. Therefore, we have determined the specific rotatory power of starch in solutions of lower concentration and have chosen that found for 1 gram of starch in 200 c.c. of solution, as the value used in the computations. We have worked exclusively with corn starch, and have made all solutions strictly in accordance with the method given in our above mentioned paper.

Using one gram of pure corn starch we found the specific rotatory power to be

Having fixed the specific rotatory power of corn starch, we began the investigation of paper. We used samples from three different batches of paper, which, through the courtesy of the Heller & Merz Co., Newark, N. J., we were able to make on their experimental machine, the exact composition being known. These three kinds of paper contained:—

| | | |
|---------------------------------|-------|-------|
| No. 1.—Sulphite Pulp..... | 1812. | grams |
| Starch..... | 181. | " |
| Water Glass..... | 181. | " |
| Alum..... | 113. | " |
| No. 2.—Sulphite Pulp..... | 1361. | grams |
| Starch..... | 136. | " |
| Rosin-Sizing from 20 gms. rosin | | |
| Alum..... | 90. | " |
| No. 3.—Sulphite Pulp..... | 1361. | grams |
| Starch..... | 136. | " |
| Alum..... | 85. | " |
| Water Glass..... | 85. | " |
| Rosin-Sizing from 20 gms. rosin | | |

The determination is carried out as follows:—

Five grams of the paper, cut into small pieces, are moistened with 20 c.c. of water, in a mortar standing in ice-water. Then 40 c.c. concentrated HCl, previously cooled in a freezing mixture, is added and the paper is thoroughly macerated with the pestle. After standing at 20°C. for $\frac{1}{2}$ hour, from the time the HCl is added, the contents of the mortar are transferred to a 200 c.c. flask (a sugar flask with wide neck is good for this), 10 c.c. of a 4% phosphotungstic acid solution are added, and then made up to the mark at 20°C. with HCl of 1.125 specific gravity. The flask is kept for $\frac{1}{2}$ hour in a water bath at 20°C. and then the solution is filtered first with suction on a Büchner funnel without any filtering medium and then through a Munktell washed filter. Exactly 15 minutes after the first filtration has been begun, the reading is taken at 20°C. in a 400 mm. tube.

DATA

| No. 1. | Temperature HCl | Temperature mixture | Reading in 400 mm. tube |
|--------|-----------------|---------------------|-------------------------|
| | | 23.0°C. | 3.0°V. |
| | +1.0 | 22.7 " | 2.4 " |
| | -4.0 | 17.6 " | 2.9 " |
| | 0. | 19.0 " | 2.8 " |
| | 0. | 18.2 " | 2.6 " |
| | 0. | 18.5 " | 2.6 " |

The readings are not concordant, due to an irregularity in the texture of the paper and probably an unequal distribution of the starch. The samples were taken from different parts of the roll. Taking the average of the readings, the per cent of dry starch was computed to be:—5.03%

| No. 2. | Temperature HCl | Temperature mixture | Reading in 400 mm. tube |
|--------|-----------------|---------------------|-------------------------|
| | 0. °C. | 20.0°C. | 3.1°V. |
| | +2.0 | 20.0 " | 3.1 " |
| | -3.0 | 23.0 " | 3.0 " |
| | 0. | 22.2 " | 3.1 " |

Per cent dry starch = 5.69%

| No. 3. | Temperature HCl | Temperature mixture | Reading in 400 mm. tube |
|--------|-----------------|---------------------|-------------------------|
| | 0. °C. | 17.5°C. | 3.2°V. |
| | +3. " | 20.5 " | 3.1 " |
| | 0. " | 21.0 " | 3.0 " |
| | 0. " | 21.1 " | 3.1 " |

Per cent of dry starch = 5.69%

One determination was made on the sulphite pulp and one, on one of the extracted residues in No. 3.

| Sample | Temperature HCl | Temperature mixture | Reading in 400 mm. tube |
|-------------------|-----------------|---------------------|-------------------------|
| Pulp | 0.0°C. | 17.5°C. | 0.0°V. |
| Extracted residue | +2.6 " | 26.0 " | 0.0 " |

This shows that there is no starch present in the pulp and that all the starch in the paper is dissolved out by this method. The residue was also tested by the iodine reaction under the microscope and showed that there was no starch present.

The above work is only preliminary, but the authors intend to carry it further and to determine the specific rotatory power of starch in solutions of varying concentration.

THE DEVELOPMENT AND STATUS OF THE WOOD PRESERVING INDUSTRY IN AMERICA

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The literature on the subject of wood preservation in America is voluminous, but so fragmentary that a summarized review of the developments and present status of the industry is perhaps justified because of the importance of the question to scientific and commercial interests. The information available is largely in the form of association and government reports and trade journal articles; while much that would be of value is filed away in private or confidential reports of railroad companies and wood consuming concerns. There is little merit attached to a compilation of the essential facts on the subject and no opportunity for originality save in possible conclusions which may be drawn. Those intimately associated with the industry will find little of interest in a general paper on wood preservation; yet its close relation to applied chemistry gives the subject considerable importance at an international meeting of chemists, and particularly so to foreign visitors who are not familiar with conditions governing the industry in America.

Economy in the use of material should be a fundamental in manufacturing and engineering enterprises; yet in the case of wood wasteful use rather than economy has prevailed for many years. The natural timber resources of America were so great that rapid exploitation followed the development of the country as railroads were pushed farther west, with the result that enormous quantities of timber have been thrown on the market at comparatively low prices. This condition prevailed up to about a decade ago and the general acceptance of preserving process to increase the life of wood material did not occur until local timber supplies in many regions were greatly depleted and prices reached a point where longer life from the wood used was essential to efficient management.

The first attempts to increase the life of wood by chemical treatment took place about the same time that apprehension was first felt regarding the exhaustion of the natural forest resources. In fact, scanty or diminishing timber supplies, even up to the present time, have been the incitement for preservative treatment. During the early days of settlement, little or nothing was known about the enormous forest resources lying farther West, and prior to the opening up of these western regions by the railroads, it seemed apparent to a few far-sighted men that the available timber in the region already settled would ultimately become exhausted. Even before wood preservation was actually attempted in America, and as early as 1800, the Federal Government recognized the importance of certain kinds of timber, particularly white oak, red cedar and long leaf pine for naval construction, and set aside several reserves aggregating about a quarter of a million acres for naval purposes.

In 1865, or about the time the first serious consideration was given to wood preservation, Rev. Frederick Starr discussed the American forests and their preservation, and in a statement which was almost prophetic in its wisdom, said: "Like a cloud no bigger than a man's hand just rising from the sea, an awakening interest begins to come in sight on this subject (forest preservation), which as a question of political economy will place the interests of cotton, wool, coal, iron, meat, and even grain beneath its feet. The evils which I anticipate will probably increase upon us for thirty years to come with ten-fold the rapidity with which ameliorating measures shall be adopted. The nation has slept because the gnawing of want has not awakened her. She has had plenty and to spare, but within thirty years she will be conscious that not only individual want is present, but that it comes to each from permanent national famine of wood." There is probably no direct connection between the early anticipations of a timber shortage and the first attempts at wood preservation, but it is interesting that the preservative treatment of timber to increase its life was urged about the same time as forest preservation; and that they both failed of general acceptance at the time, because of the vast quantities of cheap timber available.

The first American publication of much value pertaining to wood preservation is probably a paper by John Bogart in the Transactions of the American Society of Civil Engineers, Vol. 8, January, 1879. Prior to this a Treatise on the Preservation of Timber by William Chapman, Civil Engineer, published in London in 1817, was referred to by American engineers. This latter treatise contained records of experiments with twenty-one different preservative compounds, none of which is in use to date. In 1880, the American Society of Civil Engineers appointed a committee to consider the preservation of timber, and after five years' work their report was submitted and embodied in three bulletins under the dates of July, August and September, 1885. Various miscellaneous papers and reports were prepared by different individuals and associations during the next ten years, and in 1895 appeared one of the first complete railroad reports on the subject by a committee appointed by the Association of the Transportation Officers of the Pennsylvania Railroad. During this same ten year period, or from 1885 to 1895, there was considerable actual development in the construction and operation of treating plants throughout the country.

The first recorded use of treated ties is of kyanized chestnut laid in the Northern Central Railroad in Maryland in 1838, which were still sound when examined eleven years later. Kyanized oak ties laid in the tracks of the Chesapeake and Ohio Railroad in 1840, were sound when examined fourteen years later.

The first treating plant, worthy of the name, was probably that built at Lowell, Mass., in 1848, by the proprietors of the locks and canals at that point. The plant consisted of two wooden tanks, each fifty feet long, eight feet wide and four feet deep, in which the lumber was immersed in accordance with the kyanizing process using bi-chloride of mercury. Prior to 1895, several temporary plants were constructed by railroad companies, among these being one established by the Central Vermont Railroad Company in 1856; another by the Erie Railroad in 1861, at Owego, N. Y.; another by the Union Pacific in 1867, at Omaha, and one by the Philadelphia, Wilmington and Baltimore Railroad in 1863, all of these being for the use of zinc chloride by the burnettizine process. The first perma-

inent railroad plants were built in 1875 and 1876, one being constructed by the Louisville and Nashville at West Pascagoula, Miss., and still in operation, and the other by the Houston and Texas Central Railroad Company. Both were creosoting plants.

In spite of the many attempts at wood preservations during the past forty years, the rapid and permanent developments have mostly occurred during the past ten years. In 1900, there were eleven plants in operation, while at the beginning of 1912 there were about one hundred, with several more under construction or authorized. Prior to the year 1900 the most definite developments were in the West where scarcity of timber forced the railroads to adopt measures by which longer life could be given their cross ties. We thus find that the Southern Pacific Railroad has a burnettizing plant which has been in operation since 1887, while a plant using the same process was put into service by the Sante Fe in 1885. The latter road has since adopted the Reuping creosoting process. Several commercial plants were also built in the western part of the United States prior to 1900, but the general adoption of preservative treatment throughout the United States, particularly by the Eastern railroads has all been during the last ten years.

In Canada the developments have been even slower than in the United States and it is only within the past two or three years that treating plants of any size have been put into operation. At the present time, the Canadian Pacific Railroad and the Canadian Northern either use treated ties from plants already in operation, or have arranged for the construction of plants. In Mexico and South America little or nothing has been done although some of the Mexican Railroads have experimented extensively with crude oil and several plants have been built. In South American countries there are no plants, as far as the writer's knowledge goes, but large quantities of creosoted material have been shipped from plants in the United States for use particularly in marine work.

The present status of the wood preserving industry in America is very encouraging, and although the start was long delayed much economy will result from the enormous amount of work now being done and the drain on the timber resources will be very

materially reduced. At the beginning of the year 1912, 101 plants were listed by the American Wood Preservers' Association. Of this number 25 are owned and operated by railroad companies, and 12 in addition are maintained solely for railroad work. The remainder do a general commercial business.

The industry in the United States, up to the present time, has been built up largely on railroad cross ties, yet out of the 148,000,000 ties used in 1910, according to Census figures, only 26,000,000 or about 18% received preservative treatment. This however is an increase of 275% over the number treated in 1905. During the year 1910, there were also treated approximately, 133,000,000 board feet of lumber, which represents only one-third of one per cent. of the total consumption. The total output of all treated material in 1910, amounted to slightly over 100,000,000 cubic feet, which was 500% more than was treated in 1904. To treat this amount of material in 1910 there were consumed approximately, 17,000,000 pounds of zinc chloride and 63,000,000 gallons of creosote, 71% of which was imported.

In 1911, according to statistics compiled by the American Wood Preservers' Association, a total of 110,372,660 cubic feet of material was treated in the United States, this being an increase of 10% over the previous year, and a 62% increase over 1907. Of this amount 84,672,370 cubic feet consisted of cross ties, 3,910,740 cubic feet of piling, 1,085,971 feet of poles, 10,140,474 cubic feet of paving blocks, 6,831,416 cubic feet of construction timber and 2,568,857 cubic feet of lumber and miscellaneous material. By kinds of treatment 73,558,621 cubic feet were treated with creosote, 29,501,665 feet with zinc chloride and 7,312,374 feet with zinc chloride and creosote.

The kind and character of the timber treated varies greatly in different sections of the country. In the northeastern states the bulk of the material is hardwood, including red oak, beech, birch, maple and pine which is shipped in by water from south Atlantic states. In the Lake states and the upper Mississippi Valley the cross ties treated are almost exclusively hardwood of the species above named. In the South Atlantic and Gulf states, and to some extent in the southwest, pine is used almost exclusively; while in the lower Mississippi Valley and adjacent ter-

ritory, both black and red gum are being treated with apparent success. In the West and Northwest the wood mostly largely used for treatment is red fir. Considerable difference of opinion exists as to whether the so-called sap pine is suitable for cross ties. It is used extensively by some of the railroads in the South and Southwest, where traffic is comparatively light, but the experience of the railroads in the Northwestern states, where the traffic is heavier indicates that the soft sap pine does not hold the spikes well and is not sufficiently resistant to rail cutting.

Even a summarized review of the various preservatives and processes used and their development or abandonment during the past forty years would occupy too much space and would not be of particular value. In spite of the many experiments made in Europe and the knowledge based on European experience that a very large percentage of the preservatives tried were of little or no value, American inventive spirit was not content without developing many additional methods and the Patent Office records show several hundred processes and preservatives which have been tried. The report of the American Society of Civil Engineers in 1885 treated specifically the processes which had received some recognition abroad. Those considered worthy of attention at that time and which had been tried in the United States, were the Kyanizing process, using chloride of mercury; the Bethell process, using creosote oil; the Burnettizing process, using chloride of zinc, and the Boucherie treatment, by which pyrolignite of iron or sulphate of copper was introduced into standing trees and later into cut timber.

In addition to the processes above listed there are records of American experiments prior to 1882 with some thirty-five additional miscellaneous processes. Among these we find arsenic and salt, pyroligneous acid, natural soil, red lead, fish oil and tallow, tar and cement, common salt, lime, and carbolic acid. Either because of their high cost or their failure to prove effective, practically all of these earlier processes have been abandoned.

At the present time only two standard preservatives are in general use in the United States, namely, creosote and zinc chloride. Of these creosote seems to be gaining ground steadily; while zinc chloride is used mainly in the semi-arid regions of the

middle West or in combination with creosote. It should be mentioned that the Santa Fe Railroad is making very extensive experiments with a crude oil which carries a high percentage of asphaltum. While possessing no toxic properties this oil seems to effectively close the pores of the wood and act as an inert filler against the entrance of air, moisture and fungus spores. In later experiments a mixture of natural asphaltic oil and creosote has been used. In addition to the accepted preservatives named, many manufactured preservative compounds are on the market. Most of these are intended only for superficial application with a brush or in open tanks. The claims in many cases are grossly exaggerated, but some of the preparations have merit because they contain preservatives of real value.

Although the number of accepted preservatives has been reduced to two or three, several different and distinct processes for introducing the solutions into the wood are in general use. Each of these has its ardent advocates and each depending on the conditions under which it is used, has points of merit which can hardly be disputed. In a country with such diversified conditions as the United States, it is natural that what would apply and be best under one set of conditions would not prove satisfactory under another, hence it follows that if the different processes are used or modified wisely to suit the local conditions favorable results may be expected. There are also plenty of charlatans in the wood preserving business so that from time to time consideration has to be given new forms of treatment and new processes which are worthless or hardly likely to have as much merit as the treatments which have been thoroughly tried and accepted.

As detailed accounts of nearly all existing processes are available, both in this country and in Europe, it would not be advisable to repeat the descriptions. The following table summarizes the processes now used in America. The high pressure processes are most generally used, and while the so-called open tank or atmospheric pressure and the low pressure treatments have been used quite extensively by small concerns which could not afford expensive plants, it may be expected that the pressure treatment will prevail almost universally within a short time.

The various treatments or processes now in use may be briefly summarized as follows:

| | | |
|------------------------------------|------------|--|
| High Artificial Pressure Processes | Full Cell | Bethell—creosote Burnett—zinc chloride Wellhouse—zinc chloride, glue & tannin Card—zinc chloride and creosote Crude oil—natural asphaltic oil ¹ B & M—zinc chloride & aluminum salts |
| | Empty Cell | Reuping—creosote Lowry—creosote |
| Atmospheric Pressure Processes | Full Cell | Soaking in cold preservatives Soaking in hot preservatives Alternate hot and cold treatments |
| | Empty Cell | Hot, cold and hot treatments Hot and graded cooling treatment |
| Low Artificial Pressure Processes | Full Cell | |
| | Empty Cell | |

In addition to the above, kyanizing and vulcanizing plants are still operating in New England, the latter being a rapid drying or baking process without the use of a solution.

The question of specifications and standards and many important technical points requiring consideration do not come within the province of this paper. As part of a general discussion it may be stated that zinc chloride, being a mineral salt, can be manufactured to meet definite specifications. There is little difficulty in specifying the quality of chloride desired for preservative treatment and procuring from the manufacturers the grade desired. Since crude oil is a natural product it is necessary to procure the supply from oil wells which produce the quality desired, namely, that with a very high percentage of asphaltum. The oil which has been found most suitable for preservative treatment is that known as Bakersfield oil from southern California, also from certain districts in Mexico.

¹May be considered as still in the experimental state.

In the matter of creosote specifications much more difficulty is encountered. Coal tar creosote being a by-product of a by-product, and not manufactured exclusively for preservative purposes, varies greatly in its chemical composition and except by re-distillation cannot be made up to meet too strict specifications. The consumers have rather definite ideas as to the quality of cresote desired, but unfortunately it has been necessary to base the specifications on the kind of oil available, both abroad and in this country, rather than to make arbitrary standards and expect the manufacturer to meet them.

The American Railway Engineering Association has attempted to maintain a high standard for creosote, and for some years its specifications have been the basis on which most of the oil was bought and sold. It is well understood, however, that a considerable percentage of the oil used has not met the stated requirement, and that differences in methods of coal tar distillation between individual plants and between domestic and European practice led to wide variations in the quality of the creosote produced. In recognition of this situation and owing to the enormous increase in the consumption of creosote and the apparent scarcity, the Railway Engineering Association within the past year added two additional grades to the original specifications. These are intended to cover oil somewhat poorer in quality, which it is necessary for the consumers to use in order to procure an adequate supply when grade No. 1 is not obtainable, or in cases where a second grade oil will serve every purpose, as in temporary work. In the same re-drawing of specifications the character of the coal tar from which creosote may be derived was more definitely stated. It is unnecessary to quote or copy these specifications because they are available and well known, and the specific points regarding creosote standards belong to a discussion of the subject from the chemical standpoint.

Several additional problems relating to the use of creosote as a preservative are pressing for solution. These include the advisability of using various mixtures of creosote and other products such as filtered tar, water gas oil, or the combining of creosotes of different grades; the use of water gas creosote either

alone or in combination with pure coal tar creosote; the value and possible use of oil from coke over tar; and the combined use of creosote and crude oil. Another problem is that of developing methods by which adulterants may be more readily detected both in a commercial and laboratory analysis, or at least, a standard method suitable for general use.

Much remains to be done in the way of setting more definite standards both for processes and preservatives. The United States is fortunate in having a government laboratory at Madison, Wisconsin, where a large amount of most excellent experimental work is under way, and from which definite results of very great value to the industry have already been procured. In addition to this there is a large number of individual and corporation investigators throughout the country, and it may be expected that before many years much of the confusion arising from different specifications and standards will be done away with.

The mechanical equipment of the modern American plant leaves little to be desired. High pressure cylinders six or seven feet in diameter and up to 150 feet long are practically the standard. Labor saving devices are in much more general use than in Europe, and hand work is reduced to a minimum. One of the important recent improvements is an arrangement whereby the measuring and working tanks are mounted on scales, so that the amount of creosote or other solution absorbed is measured closely by actual weight rather than by volumetric scale readings. Automatic devices for unloading full tram carloads, and machines which adze, bore, saw to even length and stamp with the date, ties before treatment, are included among the mechanical developments.

The present status of the wood preserving industry in America is the result of a normal growth, which during late years, has been very rapid. Much of the educational work has been done, and nearly all large wood consuming corporations now readily accept preservative treatment not only as a matter of economy but of necessity. The present tendencies seem to be toward co-operation and greater harmony between the many interests involved. The air of secrecy which formerly shrouded the

operation of many plants has largely disappeared, and more open discussions and frank statements regarding the work are apparent. The American Wood Preservers' Association, with a large and rapidly increasing membership, is doing much toward bringing together the various interests and securing greater co-operation. The railroads, which have been the pioneers in preservative work, have for many years investigated and reported upon the subject to the American Railway Engineering and other railroad associations. More recently the lumbermen, through their interest in the production of material for treatment, are taking an active interest in wood preserving matters. As a means of disposing of inferior products and broadening the market for all forms of wood material, preservative treatment occupies a very important place. The start has already been made by some western lumber companies in building and operating plants of their own.

Wood preservation has a very far reaching effect on the conservation of our national forest resources. At present it is one of the strongest factors in the reduction of our annual timber bill, which including lumber and wood in all forms, reaches an enormous total equivalent to at least one hundred billion board feet, worth over one and a quarter billion dollars at point of manufacture. Preservative treatment reduced the drain on the forests by increasing the life of timber so that the consumption is greatly lessened. Not only this but it permits the use of many inferior woods which would be useless without treatment. As a striking example, the eastern railroads had largely exhausted the supply of durable white oak and cedar cross ties adjacent to their lines. White oak and long leaf pine when shipped long distances, became very expensive and the railroads were almost forced to develop other sources of supply. Most of the cheaper woods still available locally, were non-durable species, such as beech, maple, sap pine, etc., and it was only upon the adoption of preservative treatment that these woods could be utilized and the local cross tie supply of treatable woods drawn upon. Owing to the comparatively low freight rates on ties shipped from southern ports, pine will continue to be used by the northeastern railroads which have rail connections on tidewater. While long

leaf pine ties under rigid heart specifications have become expensive, treatment will permit the acceptance of long leaf with more sap wood. This class of ties costs less, is hard enough to wear well if laid with tie plates, and serves to augment the local supplies of broad leaved woods.

Aside from cross ties treatment makes possible a change in the character of construction timber used. For example, long leaf pine has become practically a standard in wood bridge and trestle construction and when used untreated it was necessary to have expensive heart pine which resisted decay. By creosoting or other forms of treatment it is now possible to use timber with a larger percentage of sap, and therefore cheaper and more readily obtainable. Since decay is prevented the preserved timber does not suffer loss in strength for many years, thus permitting the use of a lower initial factor of safety.

It is very difficult to estimate for the country as a whole the saving from the use of treated material, because of the great variety and complex character of the timber used. Forest Service Bulletin No. 78, however, approximates the saving in a statement that "nearly two billion feet board measure of structural timber are destroyed each year in the United States. . . . If all the timber were treated which it is practicable to treat and which could be treated at a profit, nearly six billion feet board measure or sixty per cent. would be saved. This saving would represent the annual growth on twenty million acres of well-stocked timberland." In cross ties alone the government estimates that proper preservative treatment would reduce the annual cut to the extent of nearly sixty million ties per year, which is equivalent to two billion board feet.

The present tendencies in the character of treatment are towards lighter impregnation with creosote, except in marine work and construction timber, or the use of mixtures which reduce the initial cost. No less than sixteen of the plants listed by the American Wood Preservers' Association use a light impregnation creosote process and probably as many more use it on at least part of their material; while several more plants use zinc chloride and creosote in mixture. This means that a large percentage of the treated cross ties used by the railroads have

less than six pounds of oil per cubic foot. Actually they have more than six pounds in the treatable or sap portion of the ties because the absorption is figured on the gross cubic contents. It may be argued that these light treatments are poor economy in the long run, and it is indisputable that they have not had the test of time. It must be remembered, however, that wear under the rail is responsible for a large percentage of tie failures after five years and that full impregnation would certainly not be justified without large and expensive tie plates and screw spikes. Recent developments in the adzing and boring of ties before treatment promises a solution of the question of mechanical wear in relation to impregnation and decay.

Apart from the many details which are in a fair way of being worked out, there are two very broad problems which confront the wood preservers of America, and to which they should give their attention if the industry is to remain permanent and profitable. One of these is the source of supply for creosote oil, the present indications being that a shortage is imminent and that high prices will prevail. While the consumers can perhaps do little of themselves to stimulate production, they can at least co-operate with the manufacturers and encourage the construction of by-product ovens in America, and maintain trade relations which will guarantee to the European distillers a definite market for their available creosote. Enough creosote is burned in the bee hive coke ovens of the United States every year to supply all reasonable demands for years to come.

The other problem is that of timber supply and it is one to which the wood preservers have paid too little attention. This applies to the owners of commercial plants, and particularly to the large railroad companies which either operate their own treating plants or have their work done by contract. At the present rate of increase, the cost of treatable cross ties and other material will, in a very short time, be equal to that of white oak and other more durable woods. There are still enormous supplies of cheap woods available, and it is for this very reason that steps should be taken to perpetuate the supply. In some regions, however, the supply of treatable timber is already becoming depleted, and many plants will have to seek new locations or

have their material shipped long distances within the next ten or twenty years.

Most of the hardwood timber, suitable for treatment, is of such slow growth that under present conditions it would not be profitable to reproduce it under any system of forest arrangement. In the South, on the other hand, are several fast growing trees which would respond very readily to a system of conservative management. In the loblolly pine belt, for example, the output of timber from a definite area could easily be made permanent. It is estimated that about one hundred thousand acres of well stocked loblolly pine land would produce 1,000,000 ties per annum for all time. It would have been very easy at the time some of the first railroad plants were built to have acquired timber lands at comparatively low cost and by proper management made them a permanent source of cross tie supply. This has not been done.

The railroads and other wood consumers are even now facing a distinct timber supply problem. Broadly considered, a treating plant should have back of it a definite source of timber supply, since as long as it depends on the local producers or on the middlemen for the timber used, fluctuating prices will prevail and there will be no assurance that the investment will be permanent.

COMBINIERTE MINERAL-STÄRKELEIMUNG FÜR DRUCKPAPIER

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Harzleim kann bis jetzt zum Leimen von Schreibpapier nicht ersetzt werden, für Druckpapiere jedoch sind verschiedene Vorschläge gemacht, von denen die sogenannte Mineralische Leimung nach Dr. Paul Klemm am meisten erwähnenswert ist.

Jedes Colloid ist für diesen Zweck verwendbar, wenn es nach dem Eintrocknen bindende Eigenschaften besitzt.—Das getrocknete Leimungsproduct muss derart beschaffen sein, dass es geschmeidige Eigenschaften aufweist und nicht ähnlich wie ein Füllstoff zu einem Pulver zerfällt, wie zum Beispiel auch Wasserglas, durch Alaun ausgefällt.

Dr. Klemm erzielt allein durch Verwendung von bestimmten Silicaten unter besonderen Bedingungen derartige Leimung für Druckpapiere. Verfasser erreicht diese Leimung für Druckpapiere unter gleichzeitiger Erhöhung der Festigkeitseigenschaften und erhöhtem Glanz der Oberfläche durch eine Combination von aufgekochter Stärke mit Wasserglas oder anderen wasserlöslichen Silicaten.

Folgende Erwägung liegt der Reaction zu Grunde: Gequollene Stärke als Zusatz in den Holländer kann praktisch kaum ausgefällt werden, da die niederschlagenden Agentien durchweg zu kostspielig sind. Wenn nun ein Stärkekorn durch Kochen in wässriger Lösung aufquillt, so absorbiert es Wasser unter Volumenvergrösserung, dies ist dann wasserlöslich.

Starke mit Silicaten aufgekocht, bedeutet, das Stärkekorn absorbiert neben Wasser auch Silicat, das durch nachherigen Alaunzusatz nicht allein das Silicat, sondern zugleich auch die Stärke mit ihm ausfällt, wodurch die Ausbeute von Stärke im Papiere erreicht wird.

Durch Alaun, Aluminiumsulfat oder andere ausfällende Agen-

tien wird das Aluminiumsilicat in Combination mit der Stärke als ein Colloid ausgefällt, das bei der Leimung von Druckpapier zwei Functionen versieht—erstens Fasern hart und fest macht, indem es z. T. von diesen absorbiert wird—zweitens als Bindemittel und endlich auch als Träger für alle in Suspension befindlichen Teilchen dient. Solche Teilchen sind fein gemahlene Fasern und Faserfragmente, Füllstoffe, Pigmentfarben und bei jeder Harzleimverwendung, insbesondere beim Leimen von Schreibpapieren ausgefällte Harzkörper deren Ausbeute bei dieser Reaction bedeutend erhöht wird. Die Folge des Festhaltens der eben erwähnten Teile ist ein mehr geschlossener Bogen mit gleichmässiger Oberfläche.

Während Harzleim beim Ausfällen mit selbst nur schwach eisenhaltigem Wasser harzsaurer Eisen ins Papier bringt, das lichtempfindlich ist und das Papier vergilbt, fällt dies bei der Stärke-Silicateleimung fort. Ein weiterer Effekt physikalischer Natur wird erzielt, dass so geleimtes Papier fette Druckfarbe schnell absorbiert und bei der homogenen Oberfläche die feinen Abdrücke, Halbtöne der modernen Clichés leichter aufnimmt.

In zwanzig verschiedenen Staaten der Union, in Deutschland und Italien wurden insgesamt mehr als 100 verschiedene Papiere Mineral-Stärke geleimt hergestellt.

Solche Druckpapiere, nicht allein im Holländer geleimt, sondern auch Kunstdruckpapiere nach einer ähnlichen Reaction präpariert, wurden von verschiedenen Papierfabrikanten nach Angaben des Verfassers hergestellt und Druckern in Berlin und Magdeburg, Chicago, New York und Boston zum praktischen Beurteilen gegeben, deren Resultate übereinstimmend wertvoll für die angewandte Reaction sind.

(*Abstract*)

SUGAR AND ACID CONTENT OF AMERICAN NATIVE GRAPES

WILLIAM B. ALWOOD

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This paper presents the average composition of eight varieties of grapes, viz: Catawba, Clinton, Concord, Cynthiana, Delaware, Iona, Ives and Norton, sampled in the Northern Ohio grape district and also a portion of them at Charlottesville, Va. The analyses comprise determinations for specific gravity, total solids, sugar free solids, sugar as invert and total acid as tartaric. Also, an acid-sugar ratio is given for the results for each year. The purpose of the investigation is to determine the quality of American Native Grapes as food and for the manufacture of by-products. This work has been in progress since 1908 and in most instances a large number of samples have been analyzed, thus giving to the data presented a fairly reliable character. The data of the analyses is presented in full tabular form.

The composition of these varieties of grapes as to total sugar content is very favorable and shows that American Native Grapes are as rich in sugar as the average wine grapes of Europe. The analyses given show that the variety known as Ives is the poorest in sugar, ranging from 14.75 grams to 16.12 grams sugar per 100cc. of must; that Concord is next poorest in sugar, ranging from 16. to 18. grams sugar per 100cc. of must. Catawba, Clinton, Cynthiana, Iona and Norton are very similar in sugar content, ranging from 18. to 25. grams per 100cc. of must; the latter figure is very exceptional. Delaware is the superb American grape and ranges from 20. to nearly 26. grams of sugar per 100cc. of must.

The acid content of these varieties is, however, not so favorable. The data shows that Delaware, Concord, Iona and Ives are the lowest in acid, ranging from .467 grams to .869 grams per

100cc. of must. These amounts of acid are favorable for manufacturing purposes. However, Catawba, Clinton, Cynthiana, and Norton run higher in acid content. The extreme ranges are between .712 grams to 1.918 grams per 100cc. of must. This latter figure is exceptional. All of these varieties except Clinton show an acid content below 1. gram per 100cc. of must for about half the years covered by the investigation. These results make it necessary to take into consideration methods of correcting the acidity of by-products made from the more acid varieties of these grapes, except in the best years. These data show that well ripened fruit of the American Native Grapes are much richer in sugar than has been generally claimed and that amelioration or alteration of the acid content of by-products made from them should be carefully controlled to prevent adulteration.

(Abstract)

THE COMPOSITION OF PURE WINE FROM AMERICAN NATIVE GRAPES

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This paper deals with experiments on the manufacture of straight wines from eight native American Grapes. The purpose of the experiments is to ascertain the facts in regard to the composition of the pure wine after it is fermented to dryness. The fruit used for the wines was analyzed for sugar and acid and the wines made from each sample during the several years were analyzed as young wines shortly after the period of rapid fermentation, and then again a year or more later after the wine had become dry. These analyses are presented in tabular form. The experiments have been carried on for a period of four years.

The chemical data show that these pure wines are high in alcohol except in one sample of Concord and three samples of Ives. However, in these cases the alcohol in no instance falls below 7.5 volume percent. The total acid content of many of these wines runs above .7 grams per 100cc., which is rather more than is agreeable in a potable wine. However, the alcohol being in most cases rather high the resultant acid-alcohol ratio brings the greater number of these samples well within the limit of European wines.

Some of the wines made in these experiments are in fact strong, heavy bodied wines which compare favorably with choice European samples. For instance, Delaware in these experiments produced wines averaging about 13.5 volume percent of alcohol and the acid ranging from .58 to .60 grams per 100cc., thus giving an acid-alcohol ration of about 1:22.0, which is a very acceptable ratio indeed. Cynthiana and Norton also show in these experiments, strong, rich wines with alcohol ranging from 11 to 13

volume percent, but the acid in all but two of the five samples runs above .7 grams per 100cc., thus making these wines rather acid, but at the same time demonstrating clearly that only a slight amelioration is necessary to bring the acid into the proper ratio with the alcoholic strength for a potable wine.

The chemical data is presented in detail with sugar-acid ratio of the fruit used, acid-alcohol ratio of the wine produced, and also sugar-alcohol ratio based on the total sugar of the must and the alcohol produced in the wine.

THE APPLICATION OF THE MASH-FILTER TO THE PRODUCTION OF INFUSION BEERS

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For a long time it has been very apparent to brewing experts that the mashing operations as conducted in the great majority of breweries working on infusion lines are crude and wasteful, and this fact has been gradually brought home to a considerable number of Brewers. At the present moment the great majority of brewers in this Country are carrying out their mashing process in a manner differing but little from that adopted a century or more ago. For this somewhat extraordinary state of affairs, there are perhaps two main causes. In the first place the brewing industry has been on the whole a very profitable one, and brewers have had no special incentive to experiment with new appliances and unfamiliar methods, even when these promised to be more efficient and more economical in working.

In the second place brewers have firmly believed, as many do still, that it is a mistake to get "too much out of the malt." Although I have never succeeded in getting any trustworthy evidence in support of this somewhat widely spread belief, it is quite easy to see how it originated. At a time when the science of melting was practically non-existent, a great deal of malt was steely and badly modified, and when such malt was submitted to high sparging temperatures in the hope of getting more extract, the resulting worts would almost certainly contain starch and other imperfectly modified matters, greatly to the detriment of the resulting beer. At the present time, owing to the great advances which have been made in the technology of malting, and to our greatly increased knowledge of the scientific principles underlying the mashing process, such results are almost inconceivable, and brewers are rapidly becoming alive to the fact that even if it should be a mistake to get too much out

of the malt, it is a far more serious mistake to get too little. This process of education has doubtless been accelerated by the heavy fiscal burdens which the industry has been called upon, during recent years, to bear, and by trade competition, which is daily becoming more severe. The brewer of to-day is, in fact, beginning to realise that if he is to maintain his position in the struggle he, like other technologists, must take advantage of every improvement, either in plant or in procedure, which makes for greater efficiency and increased economy.

In no part of the brewing process is there so much room for improved technique and increased economy as in that which is concerned with the making of the mash, and it is with this that we propose to deal very briefly in this communication. It is to be understood at the outset that my remarks have reference almost entirely to the infusion system of mashing as adopted in England and in many American Breweries, and that they do not apply with anything like the same force to decoction or even to semi-decoction mashing.

Intimately connected with the process of mashing, is the process of grinding, and it is therefore necessary in the first place to refer to this. In its simplest form a malt mill consists merely of a single pair of rolls, but it is abundantly evident that with such a mill, it would be impossible under ordinary circumstances, to obtain a grist suitable for infusion mashing. If on the one hand the rolls were set sufficiently close to crush the thin corns which are always present, the whole of the grist would be so fine that mash-tun drainage would be seriously impeded, and in bad cases a "set mash" might result. If on the other hand the rolls were set at such a distance that a grist was obtained capable of giving a buoyant and porous mash then the smaller corns would escape crushing entirely and a very serious loss of extract would be incurred. In order to avoid this difficulty, a type of mill has been very widely adopted consisting of two pairs of rolls set side by side, the rolls of the one pair being set rather closer than those of the other. By means of grading machinery the malt is then separated into large and small corns, the former going through the rolls of wider gauge, and the latter through those which have been more closely set. In this way something

like uniformity of grind is obtained, and assuming that the malt with which the Brewer has to deal is very friable and thoroughly well modified, the results for extract yield are good. Such, however, is very rarely the case, the great majority of Brewers in England and in other Countries having to deal with grain which, owing, perhaps to bad harvesting conditions or to improper treatment on the malting floors, is stubborn and difficult of conversion, and the difficulty is, of course, greatly increased when certain hard foreign malts, such as Ouchac, have to be used. In such cases a Brewer adopting the infusion system is always between the horns of a dilemma. If he just crushes or grinds very coarsely, the hard-ended and gritty portions will escape modification, whereas if he grinds finely, the mash will not drain properly, and loss of extract will result. This is the problem to the solution of which Brewers' Engineers have for some years devoted their attention, and it is satisfactory to record that several firms have been successful in designing grinding machinery which leaves very little to be desired. One of the best known of these improved mills is the Seck Mill, which consists essentially of two pairs of steel rolls, one pair placed above the other. Between them there is an oscillating sieve which separates the crushed corns from the first pair of rolls into husk on the one hand and grits (together with some flour) on the other. The husks with any imperfectly modified hard-ends are then passed through the lower rolls, after which the products from both pairs of rolls are mixed together, a grist being thus obtained, in which the starchy portions of the grain are reduced to a tolerably fine state of division without any undue breaking up of the husk. In the case of very steely malt, provision is made by means of a switch for the alteration of the position of the sieve, so that coarse grits from the first pair of rolls can be passed through the second pair in order to secure finer grinding, which is very necessary in the case of such malts, if anything like the full extract is to be obtained with an ordinary infusion system. To attain this end in a more perfect manner, a three-pair roller mill has been devised by the same Firm, in which the large steely grits, after having been separated from the husks, can be passed through an additional pair of rolls.

Mills based on somewhat similar principles have been constructed by other firms, but it would serve no useful purpose to describe these in detail, particularly as they are not specially designed for the production of fine grist such as is necessary in connection with the use of the mash filter. Mills such as these fulfil the conditions indicated above,—that is to say, they convert the grain into a grist consisting of uniformly small grist with the minimum amount of flour and large flaky unbroken husk. It is, therefore, possible to derive the full advantage from the husk in keeping the mash porous and buoyant, whilst at the same time the starchy portion of the grain will have been reduced to such a fine state of division as to render its saccharification nearly complete under the ordinary conditions obtaining in the infusion mash-tun. It will be readily understood that the advantages of these improved separating mills are greater in proportion as the grain which has to be used is hard and badly modified. I have already pointed out that with very friable and tender grain, an ordinary double roller mill is capable of giving very fairly satisfactory results, but it is when using hard foreign material such as Ouchac, Indian, etc., and grain in which the modification changes have been incomplete, that the full benefits are obtained. I have, for instance, found that the grist from a very hard foreign malt was capable of yielding, when ground in one of these mills, an extract which was only 2 lb. per standard quarter less than the maximum extract yielded by decoction mashing, whilst with ordinary grinding the extract was five pounds lower still. There are obviously two methods of ascertaining whether the brewer is getting from his materials the amount of extract which he ought to obtain. The one involves a comparison of the working yield with the theoretical yield based upon an analysis of all the materials employed. The other method is to examine the residual mash-tun grains and so ascertain what amount of starch is being actually lost. The former, which is somewhat widely adopted, has the very serious disadvantage of involving certain assumptions. It has to be assumed, for example, that the small samples as analysed in the laboratory actually represent bulks as used in the brewery. It has to be borne in mind, moreover, that the laboratory ex-

tract of a sample of malt is a very indefinite number, and that it is difficult, without a good deal of experience of the working of some particular brewery to arrive at any definite relationship between the laboratory extract obtained with standard grinding, and the yield which should be got in that brewery. The examination of the mash-tun grains on the other hand, affords perfectly definite information, and I am strongly of opinion that this is an estimation which ought to be frequently made in all brewery laboratories. With a well constructed mash-tun, working on the simple infusion system as practised in this Country and using well modified and tender malt, ground in an ordinary double roller mill, the residual starchy and other extractive matters (expressed on the dry grains) will rarely, if ever, fall below 5 per cent. In many cases I have found numbers as high as 8 per cent and in bad cases as much as 15 or even 20 per cent. Of course, when numbers such as the latter are in question, the brewers' extracts are so much below the average that the loss he is incurring is brought home to him in a forcible manner, and steps are immediately taken to put matters right. In the great majority of cases, however, the loss is not, perhaps, sufficient to force itself on the Brewer's notice, and a Brewer who works in a rule of thumb manner or who is not alive to the necessity of putting his operations under scientific control, may, unknown to himself, be losing an amount of extract which, in the aggregate, may be quite serious. I shall most certainly be on the safe side if I say that in England at the present moment, there are very few breweries indeed where at least an extra pound of extract per standard quarter could not be obtained, and this in a comparatively small brewery, say with a 50 quarter plant brewing six times a week, would mean a saving of more than £300 per annum, whilst in a very considerable number of breweries, the saving would be very much greater.

From what I have already said, it will be gathered that with an infusion system the extract yield is dependent in the first place on the grinding, and in the second, on the mashing operations and plant. These two questions are to a certain extent, interdependent, but I may point out that in a number of breweries I have observed a considerable increase in the extract yield

obtained from a certain run of materials without any change in the mash-tun procedure and solely as the result of substituting one of the above mentioned perfected separating mills for the ordinary simple type. In illustration of this, the following results, which are typical of a good many I have obtained, may be of interest. Of these numbers, which represent in all cases the percentages of starch and other extractive matters (expressed on the dry grains) left in the mash-tun of a certain brewery, the first seven correspond with ordinary grinding, whilst the last five were subsequent to the introduction of a separating mill:-

8.5%
11.7%
4.9%
8.6%
11.2%
6.3%
7.7%

4.3%
4.3%
3.8%
3.8%
3.2%

It will be seen that the mean of the first seven numbers is 8.4, and that of the last five, 3.8. In this brewery, the malt used consisted of about 70 per cent of medium grade English and 30 per cent of Ouchac. The average increase in extract yield as the result of adopting the more perfect type of mill amounts to no less than 4.6 lb. per standard quarter, or approximately 3.5 per cent of soluble solids. Assuming a consumption of only 10,000 quarters of malt per annum, this would amount to a saving of approximately £1000.

I will now pass to the consideration of the use of the mash-filter. Whilst perfected separating mills of the type above

mentioned enable a very much larger amount of extract to be obtained than would otherwise be the case, there must still be a certain amount of loss, since it is not feasible, even when the husks remain practically intact, to obtain satisfactory mash-tun drainage with the starchy portions ground to the condition of flour.

From the results I have given above, it will be seen that even with the most perfect grinding obtainable, the mash-tun grains contain approximately 4 per cent of starchy and other extractive matters expressed on the dry grains, which of course represents so much extract lost to the Brewer. About the year 1900, M. Meura conceived the idea of substituting a converter and a filter press for the ordinary mash-tun. Notwithstanding the fact that this early filter press possessed certain defects of construction the advantages of the process were so considerable that the Meura plant found its way into a good many Continental Breweries and received the high commendation of a number of brewing experts. Owing to the conservatism of English Brewers, the method did not obtain a footing in this Country, despite the very favourable reports from the Continent, until the year 1903, when mash-filters were installed in two English Breweries belonging to the same firm. In the one Brewery it was used solely for the purpose of filtering a raw grain conversion, whilst in the second Brewery it was used for the filtration of the whole mash. As I have indicated above, the original Meura Filter was not altogether satisfactory, and improvements were effected by J. G. Crossman who succeeded in considerably increasing the capacity of the chambers, so that whilst a Meura Press capable of dealing with a 20 quarter mash had 56 chambers, the Crossman press having an equal capacity had only 35. Other improvements in connection with the method of washing the grains and of fitting the filter cloths were also made, and this improved press was found to perform its work in a very satisfactory manner. The following are the essential features of a mash-filter process:-

1. Very fine grinding.
2. The employment of an improved mashing apparatus of the converter type; and

-
3. The employment of a special form of mash-filter in which the wort is separated from the insoluble portions of the grain and in which rapid and thorough washing can easily be carried out.

With regard to the second point, it may be mentioned that an ordinary mash-tun can often be adapted, but for several reasons a converter is preferable, as it ensures a more perfect command over the temperature and enables the Brewer to deal satisfactorily with larger proportions of grain adjuncts than would otherwise be the case. With fine grinding and proper conversion, the amount of residual starch in the pressed grains is invariably under 1 per cent, and sometimes only amounts to a trace, so that it is clear that even with the most perfect grinding, there exists in the grains taken from the ordinary mash-tun between 3 and 4 per cent of starch (on the dry substance) which would be obtained as extract if a mash filter process were adopted. Putting this in other words, it may be said that the increased extract yield obtained by the employment of such a process amounts at the very least to from 1 to 2 pounds per barrel per standard quarter, and that when low grade malt is employed or when large proportions of raw grain are used, the increase would be considerably greater. The washing of the residual grains in the filter chambers can be carried out with great thoroughness, the last runnings being almost invariably under 1001°. This I have ascertained for myself on a number of occasions, and I have also found that portions of the cake taken from the extreme corners of the frames were washed to practically the same extent.

I may perhaps summarise the various advantages attaching to the mash-filter system of brewing under the following headings, merely adding that each of these statements is made as the result of my own observations, and that they are endorsed by a number of experts both in England and on the Continent:-

1. Increased extract yield.
2. Shortened working day.
3. A reduced fuel bill.
4. The possibility of using larger proportions of raw grain with ease and certainty of result.

5. The possibility of obtaining full extracts when brewing strong beers, without the necessity of holding over worts or of making part-gyle brewings.

In regard to the first and most important advantage I may point out that a yield approximating to the total available extract is got, and hard and imperfectly modified grain can be dealt with quite easily and quite satisfactorily on infusion lines. It may be well to point out that this system does not necessitate any change in existing brewing methods other than those involved in the substitution of perfected and efficient mashing and filtering appliances for a piece of plant which has long been known to be inefficient and wasteful. The shortening of the working day is also a matter of very considerable importance, since it has the effect of considerably increasing the capacity of any given Brewery and would in many cases do away with overtime pay. The shortening of the period necessary for the washing of the grains, obviously means a reduction of the fuel bill, since less coal would be needed to keep the washing water at the requisite temperature than would be the case with ordinary sparging operations. The proportion of raw grain which can be used in any Brewery is, of course, conditioned very largely by the requirements of the trade and the character of the beer which is to be brewed, but it is certain that with a mash filter process much larger proportions can be successfully employed than would otherwise be possible.

The above advantages are so evident that it is unnecessary to dwell on them at any greater length, and the important question that remains to be answered is whether the infusion beers produced by such a system are as good as those produced in the ordinary way. My experience, and that of several of my Colleagues, is entirely satisfactory on this point, and I have no hesitation in affirming that the beers produced by a mash-filter process are fully equal in every respect to those brewed on the older lines. I have had an opportunity of seeing this process at work in several Continental Breweries, and in every case I was informed that the beers produced were thoroughly satisfactory in respect of brilliancy, flavour and head-retaining capacity. During recent years further improvements have been made in the

mash-filter, and the Weigel press, which represents the latest serious attempt to grapple with the question of mash-filtration, leaves apparently very little to be desired in respect either of construction or working. It is within my knowledge that this press is being used with very satisfactory results in a considerable number of Continental Breweries, and in a few cases in Breweries working on the infusion system.

When I undertook to prepare for this Congress a paper dealing with the application of the mash-filter to infusion brewing, I hoped to have been able to present the results of a number of my own observations with a Weigel press. Owing to circumstances over which I had no control, this has unfortunately been impossible, but such observations are shortly to be made, and I hope to be able to deal at greater length with this subject at the next Brewing Congress. Ever since the introduction of the Meura Press I have strongly advocated the introduction of the mash-filter into English Breweries, and now that the question of fine grinding has been solved, there would appear to be no reason, other than that connected with initial expense, why the process should not make rapid headway. The plant is, of course, expensive, but the question of initial outlay has always to be considered in connection with the saving which would be effected, and I believe that in the great majority of Breweries, the plant would pay for itself in a comparatively short time.

DIE BETRIEBSWEISE DER DEUTSCHEN BRENNER-EIEN NACH AUFHEBUNG DER MAIS-CHRAUMSTEUER

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Die im Jahre 1909 erfolgte Änderung des deutschen Branntweinsteuergesetzes hat eine vollkommene Umwälzung der Technik des deutschen Brennereigewerbes zur Folge gehabt.

Seit dem Jahre 1819, also volle 90 Jahre hindurch, bildete die Grundlage der Besteuerung des Spiritus die Maischraumsteuer, d.h. also eine Steuer, welche nach der Grösse der in Benutzung genommenen Gärbottiche bemessen wurde. Eine Ausnahme hiervon machten seit dem Jahre 1887 nur die gewerblichen Brennereien, das sind vorwiegend solche Brennereien, welche Hefe erzeugen und infolge ihres besonderen Arbeitsziels von den übrigen Brennereien ganz abweichende Fabrikationsmethoden anwenden. Die grösste Menge, hämlich über 85% des in Deutschland herstellten Spiritus wird aber in landwirtschaftlichen Brennereien hergestellt, und für diese war bis zu der vor drei Jahren erfolgten Gesetzesänderung mit wenigen Ausnahmen die Maischraumsteuer obligatorisch.

Diese Besteuerungsart drängte naturgemäss dazu, möglichst zuckerreiche Maischen herzustellen und zu vergären, um den auf eine gewisse Spiritusmenge entfallenden Steuerbetrag nach Möglichkeit zu verringern. Die Verarbeitung von Dickmaischen war aber nicht nur aus wirtschaftlichen Gründen geboten, sondern erschien, sofern dabei gewisse Grenzen inne gehalten wurden, auch wissenschaftlich wohl begründet; denn in zuckerreichen, und daher auch alkoholreichen Maischen ist es unbestritten leichter, Bakteriengärungen zu unterdrücken und eine rein alkoholische Gärung durchzuführen, als in zuckerarmen Flüssigkeiten.

So war die Arbeitsweise der Brennereien allmählich immer

mehr nach der Richtung ausgebaut worden, dass aus dem versteuerten Raum möglichst hohe Spirituserträge erzielt wurden. Durch besondere Dämpf = und Maischmethoden und die Konstruktion geeigneter Apparate war man einerseits dahin gelangt, auch aus stärkarmen Rohstoffen zuckerreiche Maischen herzustellen; andererseits hatte man gelernt, durch planmässig ausgewählte Hefenrassen, sowie durch geeignete Züchtungsmethoden für die Hefe und durch besondere Gärungsführung die stark konzentrierten Maischen in der durch das Steuergesetz zugelassenen Zeit zu vergären. Die Intensität der Gärung hatte man weiter dadurch zu steigern gewusst, dass man die Maischen künstlich bewegte. Durch die hierbei stattfindende gleichmässige Entfernung der Kohlensäure aus der Maische wurde zugleich erreicht, dass der für das Ansteigen der Maische im Gärbottich zu belassende freie Raum bedeutend verringert werden konnte; schliesslich entfernte man noch durch besondere Apparate (Entschaler) aus der Maische die groben Schalen und schaffte dadurch im Gärbottich Raum für neue Mengen gärungsfähiger Flüssigkeit.

Es war uns allerdings sehr wohl bekannt, dass diese durch die Art der Besteuerung gewissermassen vorgeschriebene einseitige Arbeitsweise, was die Ausnutzung der Rohstoffe anbelangt, nicht vollkommen auf der Höhe war. So wussten wir im Besonderen, dass die Herstellung zuckerreicher Maischen gelegentlich zur Verschwendungen von Rohstoffen führte, weil mit dem Ablassen des Fruchtwassers aus den Kartoffeln beim Dämpfen gewisse Mengen von Zucker und Stärke verloren gingen; wir wussten ferner, dass durch das Entschalen der Maische gewisse Mengen gärungsfähiger Stoffe entfernt wurden, und dass bei übertrieben starker Konzentration der Maische der vorhandene Zucker während der gesetzlich festgelegten Gärdaue nicht immer vollständig in Alkohol umgewandelt wurde. Aber die Rücksicht auf die zu zahlende Steuer überwog diese Bedenken. Zum Teil unterschätzte man vielleicht die bei der Bereitung der Maische eintretenden Zuckerverluste, und bezüglich des mit den Schalen entfernten Extraktes und der eventuell unvergoren bleibenden Menge von Zucker tröstete man sich damit, dass sie direkt, oder in Form von Schlempe

dem Vieh als Nährstoffe zugute kämen. Dies war wenigstens für die landwirtschaftlichen Brennereien zutreffend, weil sie die Schalen und die Schlempe an das eigene Vie verfütterten. Immerhin war nicht zu leugnen, dass diese Zuckermengen ihrer eigentlichen Bestimmung, Alkohol zu liefern, entzogen wurden.

Es war uns ferner auch bekannt, dass im offenen Gärbottich stets gewisse Alkoholmengen durch Verdunstung verloren gingen; es war deshalb oft erwogen worden, bedeckte oder geschlossene Gärbotitche zu verwenden, doch war dies nach dem Steuergesetz nicht zulässig. Wir waren endlich nicht darüber im Unklaren, dass die Verdunstungsverluste durch eine starke Bewegung der Maische noch vergrössert wurden. Indessen war es für den Praktiker schwierig, sich von der Grösse dieser Verluste in der Parxis ein zutreffendes Bild zu machen und da durch die künstliche Bewegung der Maische der Alkoholertrag vom versteuerten Raum unzweifelhaft erhöht wurde, so überwog dieser in die Augen fallender Nutzen alle Bedenken, welche sich gegen die Bewegung der Maische erheben liessen.

Die Aufgabe, unter allen Umständen hohe Spirituserträge vom versteuerten Raum zu erzielen, war den deutschen Brennern derart in Fleisch und Blut übergegangen, und die Mehrzahl der Brennereitechniker war dermassen von der Ansicht durchdrungen, dass die Jahrzehnte lang angewandte Arbeitsmethode technisch in jeder Beziehung auf der Höhe war, dass viele von ihnen, als der durch das Steuergesetz ausgeübte Zwang, Dick-maischen zu verarbeiten, fortfiel, zunächst nicht einsehen mochten dass eine Aenderung der Arbeitsweise eine bessere Ausnutzung der Rohstoffe zur Folge haben könnte. Nur zögernd und allmählich wurde deshalb die vom Institut für Gärungsgewerbe nach dem Inkrafttreten des neuen Branntweinsteuer-gesetzes ausgegebene Parole befolgt, welche für die zukünftige Arbeitsweise nachstehende Grundsätze aufstellte:

1.) Bei der Herstellung der Maische sind alle Massnahmen, welche Zuckerverluste verursachen können, zu vermeiden, d.h. bei der Verarbeitung von Kartoffeln ist das Ablassen von Fruchtwasser zu unterlassen oder möglichst einzuschränken, und das Entschalen der Maische ist darauf zu beschränken, dass nur die groben Schalen, welche eine Verstopfung der Ventile

der Pumpen oder des Destillierapparates verursachen können entfernt werden.

2.) Die Konzentration der Maischen, welche bisher 23–26 Grad Balling, entsprechend einem spezifischen Gewicht von 1,11–1,10, zu besitzen pflegten, ist auf 19–21 Grad Balling, entsprechend einem spezifischen Gewicht von 1,08–1,09 herabzusetzen.

3.) Die Gärbottiche sind nicht mehr, wie bisher üblich, möglichst bis zum Rande zu befüllen, vielmehr sind die Maischen durch ein hohes Kohlensäurepolster von der atmosphärischen Luft nach Möglichkeit abzuschliessen. Zu dem Zweck sind die Gärbottiche während der Gärung zu bedecken; noch besser ist es, die Gärung in vollständig geschlossenen Gärbottichen verlaufen zu lassen.

4). Die künstliche Bewegung der Maische während der Gärung ist—zum mindesten in offenen Bottichen—zu unterlassen.

Die Erfahrungen, welche in den drei Jahren seit der Einführung dieser Arbeitsweise gesammelt worden sind, haben nunmehr bewiesen, dass wir mit unseren Vorschlägen durchaus das Richtige getroffen hatten. Ja ich kann sogar zu meiner Freude berichten, dass unsere kühnsten Erwartungen noch übertroffen worden sind, denn die Mehrausbeuten an Spiritus aus den eingemaischten Rohstoffen, welche auf dem angegebenen Wege erreicht werden, betragen rund 10%.

Diese beträchtliche Mehrausbeute findet ihre Erklärung in folgenden Umständen:

1.) Die Zucker = und Stärkeverluste, die bei der Herstellung von Dickmaischen einzutreten pflegten, werden vermieden und alles in den Rohstoffen enthaltene gärungsfähige Material gelangt in den Gärbottich.

2.) In den wesentlich dünneren Maischen wird die Stärke, selbst bei geringerem Malzverbrauch, vollkommen gelöst und besser verzuckert.

3.) In den dünneren Maischen bleiben geringere Zuckermengen unvergoren.

4.) In den bedeckten oder vollkommen geschlossenen Gärbottichen verläuft die Gärung äusserst rein, obwohl der geringere

Alkoholgehalt der dünneren Maische einen weniger wirksamen Schutz gegen das Aufkommen von Bakterien gewährt.

5.) Alkoholverluste durch Verdunstung werden in den bedeckten Gärbottichen vermieden, oder wenigstens wesentlich eingeschränkt; bei Verwendung geschlossener Gärbottiche werden auch die mit der Kohlensäure als Dampf entweichenden Mengen von Alkohol gewonnen.

Welcher Anteil der Mehrausbeute an Alkohol auf die einzelne Punkte entfällt, lässt sich durch allgemein giltige Zahlen schwer angeben, weil dies von der früher angewandten Arbeitsweise abhängt.

Beispielsweise wird der Gewinn an Alkohol durch Verhütung des Verdunstung in denjenigen Brennereien besonders gross sein, in denen man bisher flache Gärbottiche mit verhältnismässig grosser Oberfläche anwandte; das gleiche ist der Fall in solchen Brennereien, in denen die Maische während der Gärung hohe Temperaturen erreichte. Ebenso ist die Menge Alkohol, welche durch Waschen der Kohlensäure gewonnen wird, umso grösser, je höher die Gärtemperatur, und je grösser der Alkoholgehalt der Maische ist.

Die Methode der Hefenbereitung ist durch die Aufhebung der Maischraumsteuer nur wenig beeinflusst worden; man verwendet für die Hefe nach wie vor mit Vorliebe möglichst konzentrierte, d.h. so zuckerreiche Maischen, wie sie bei der jetzigen Bereitung der Hauptmaische herzustellen möglich sind. Im übrigen erfolgt die Hefenbereitung nach den Grundsätzen der natürlichen Reinzucht, d.h. man benutzt als Anstellhefe zwar Reinzuchthefe, aber es kommen weder absolut sterile Maischen noch Hefen in absoluter Reinzucht zur Anwendung. Trotzdem verläuft die Gärung, wie die Erfahrung lehrt, in den geschlossenen Bottichen in ausserordentlicher Reinheit. Meines Erachtens ist der Erfolg, den das bekannte, besonders in Maisbrennereien angewandte, Amylo=Verfahren aufzuweisen hat, auch nicht in erster Linie auf die vollkommen aseptische Arbeitsweise, sondern darauf zurückzuführen, dass es schwach konzentrierte Maischen verwendet und diese in geschlossenen Bottichen vergären lässt.

Den Wert des Arbeitens mit vollkommen sterilen Maischen

und mit Hefen in absoluter Reinzucht will ich damit keineswegs herabsetzen; ich halte es im Gegenteil für sehr wohl möglich, dass damit noch etwas höhere Alkoholausbeuten zu erzielen sind, als sie sonst in geschlossenen Bottichen erreicht werden können. Für die Praxis kommt es aber darauf an, ob den eventuellen Mehrausbeuten nicht ausser Verhältnis stehende höhere Betriebskosten gegenüberstehen.

Bisher hat das Amylo=Verfahren in Deutschland keine wesentliche Verbreeiung gefunden, wohl aber gehen die Brennereien allmählich dazu über, die offenen Gärbottiche durch geschlossene Bottiche, wie sie das Amylo=Verfahren verwendet, zu ersetzen, und zwar macht man die neuen Gärbottiche, zu deren Herstellung Eisenblech verwendet wird, so gross, dass *ein* Gärbottich die an einem Tage hergestellte Maische zu fassen vermag.

Meines Erachtens gehört den geschlossenen Gärbottichen die Zukunft; man wird sie mit Vorteil überall dort in der Brennerei anwenden, wo es gilt, die höchstmöglichen Spiritusausbeuten aus den verarbeiteten Rohstoffen zu erzielen.

(*Abstract.*)

THE LAWS OF MAN IN THEIR RELATION TO THE
MANUFACTURE AND SALE OF PRODUCTS RE-
SULTING FROM THE NATURAL LAW
OF FERMENTATION

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Fermentation is an entirely natural process, must have been going on in nature long before man appeared, and man observed and began to use the process in very remote times, first in the transformation of grape-juice into wine. This process we now know to be the spontaneous action of the micro-organisms in the yeast-cells in the grape-juice, by which action the sugar is transformed into alcohol.

Distillation is also an entirely natural process, being merely vaporization and condensation, and occurring constantly in nature, as in the vaporization of sea water by the sun's heat and condensation as rain. Man observed and used this process and began the distillation of alcohol from wine in very ancient times.

The first uses of alcohol (spirit of wine) were as medicine, and the monks of the Middle Ages, generally skilled in this art, began to produce alcoholic liquors. These spread into use as popular beverages. The fermenting of wine and distilling of alcoholic liquors requires only the simplest sort of utensils. All the modern improvements in distilling apparatus have not changed the essential features of the process, but have greatly purified the product.

The materials for making alcoholic liquors are found in variety and abundance in practically every country and climate. With the materials conveniently at hand and the necessary apparatus easily available, men have been making and using such liquors for thousands of years. The great historical fact about such

liquors is that from their first knowledge of them human beings everywhere have constantly craved and demanded them, notwithstanding all obstacles and restrictions. This demand creates the supply, according to the economic law, which is the statement of a natural and inevitable process.

Artificial restrictions against the use of such liquors arose at an early period. The power of government and law was used against the human appetite for liquor. The first efforts were along the line of the first impulse of human nature, to prohibit the use through the overwhelming power of government. Early prohibition edicts were not effective or lasting. The system of state taxation and regulation soon came into use. Governmental law does not, like religious law, destroy the demand by affecting the judgment and conscience of the individual. Governmental laws inevitably involve constant conflict between the government and the individual, with varying success by the government according to the sort of laws it attempts to enforce.

Practically all forms of liquor laws deal with the retail sale and may be divided roughly into four classes: (1) The Licensing System, (2) the Scandinavian or Company System, (3) State Monopoly, and (4) Prohibition. The licensing system is the oldest in extensive use and most successful, and yields great revenue to governments. The other systems have decided disadvantages, and prohibition, the most extreme of all, is not effective, and its advocates claim that it is not enforced.

Official evidence shows increased illicit distillation in prohibition States of the United States, and illicit distillation means impure liquors. The advocates of prohibition confess its failure in such States and demand additional legislation. Long experience in this and other countries shows that it is so easy to make liquor that the people who demand it will not be without it, no matter what the law declares. The United States government, with the great revenue at stake, uses the greatest possible efforts to keep down illicit production. Without the revenue, no Federal or State Government could pay the expense of such service.

The advanced countries of the world, which, for the most part, use the licensing system, show a gradual lessening of the misuse

of alcoholic liquors. This is caused principally by the improved living conditions of the people and the advance of popular intelligence, resulting in greater self-control. The real way of further progress is to extend these rational methods of human betterment. Fanaticism and unreason must be overcome and it is important for all industries that the capital invested under the sanction of our laws in establishments producing fermented and distilled liquors should have fair treatment. The manufacturers using alcohol for industrial purposes would have great difficulty under the prohibition system in getting their necessary material under satisfactory conditions.

MODERN METHODS OF BREWERY REFRIGERATION

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If you expect to hear of any startling improvements over the old and known methods of Brewery Refrigeration, I fear you may be somewhat disappointed. In fact, there is very little for me to say at such a gathering of experts beyond the statement that in comparing some of the modern installations with some of the older, we find that the cheapness of the modern installation is commonly of greater importance than the practical and economical operation of the system.

To the Brewer credit must be given for paying at least the costs for developing the Refrigerating Machinery, if not actually inventing or improving the existing apparatus but at the present time very little attention is paid to any special or improved methods in Brewery Refrigeration.

In fact so little attention is given the subject today, that in a recent Annual Meeting of the American Association of Refrigeration you will find no mention of it under the heading "On the use of Refrigerating apparatus in the Industrial Arts."

It would be interesting to note however to what uses the refrigerating machines are put, according to the list as printed in the Proceedings of the American Association of Refrigeration.

1. The manufacture of ice for refrigeration, domestic uses, skating rinks and other purposes.
2. The manufacture of ice cream and ices.
3. Air drying for blast furnaces and other purposes.
4. The manufacture of petroleum products—solid, liquid and gaseous.
5. The preservation and manufacture of tobacco and its products.
6. Leather and its products, including tanning.
7. The manufacture of textile materials, including treatment of the raw material—dyeing, printing, etc.

8. Cooling and ventilating living, factory and assembly rooms.
9. Horticulture and floriculture.
10. Shaft-sinking, mining, tunneling and excavating.
11. Manufacture and storage of explosives.
12. Manufacture of fatty substances—soap, vegetable and animal oils, etc.
13. Manufacture of photographic materials and processes.
14. Rubber and its products.
15. Pharmaceutical products, including extracts, perfumes, camphor, oxygen, etc.
16. General application to mechanical and electrical work.

There would seem from this list to be more profit for the Refrigerating Machine Builders, in constructing for the Ice Cream Factories; the manufacture of Petroleum Products, Vaseline, etc., and for Rubber and its products, than for breweries.

Coming back to the subject proper and without going into the history of Refrigeration in Modern Brewery Refrigeration, the subject may be divided into—

First, the selection of available standard apparatus.

Second, the Installation of the Apparatus.

Third, the Operation.

In the selection of the Refrigerating machinery, care must be taken to select of Standard makes only such apparatus as will best suit our conditions. As for instance, a vertical compressor may fit the size and condition of the building in one case, whereas in another, a horizontal compressor may suit the conditions better. Again, for hard water a double pipe Ammonia Condenser would be more suitable, than an open, or atmospheric type of Condenser.

Again in the selection of the type, a brine system may be more suitable for a Brewery up to 100,000 Barrels output than a direct Ammonia system. The cost of labor and of Fuel, enter a great deal into the last problem.

The selection of the proper size apparatus is of great importance for economic and other reasons. As for example, a compressor much too large for its work, will waste considerable steam and oil, or insufficient ammonia condensing surface, will

raise the liquifying pressure, with a resulting waste of power. And again, insufficient cooling or heat absorbing pipes will be a double loss to the brewer, first from spoiled products, and second, from having to operate the compressor at a lower back pressure in order to produce a greater difference between boiling temperature of ammonia and cellar temperature and thereby make up the deficiency of the cooling or heat absorbing surface.

In selecting refrigerating machinery for Brewery, and other refrigeration, each case should be treated separately, and all conditions carefully considered.

In most cases, the greater part of refrigeration consists in absorbing the heat which enters through the walls of cellars or rooms, this may amount to as much as 60% of the total refrigeration.

Therefore, the better the insulation, against the heat entering, the smaller the refrigerating apparatus would have to be with the resulting economy, considering that Insulation conditions may vary from passing 12 B.t.u. in 24 hours per square foot of surface, for each degree difference in temperature between outside and inside temperature, as in a 12 inch brick wall, to 0.7 B.t.u. for a combination of brick wall, hollow tile, and cork insulation.

In selecting the proper insulation, it is of course a question of balancing the investment and deterioration of Insulation on one side, against the saving of fuel on the other side.

Then the selection of driving power for the compressor is quite a problem. With the ever advancing prices of fuel, such as coal and oil, it will make quite a difference in the operating expenses, whether we are using an Engine consuming 30 pounds of Steam per hour per horse power, as most of the best Corliss Engines require, or one which will consume 15 pounds of Steam per hour per Horse Power, as in a good compound condensing Corliss Engine, or even as low as 9 pounds of Steam, as a great many Brewery Installations in Europe can show. There, the high price of coal, as high as Seven to Eight Dollars per ton of Bituminous coal has done a great deal towards perfecting the Boilers and Steam Engines.

To obtain such results it is necessary to use high pressure, superheated steam; Engines designed for high pressure and super-

heated steam and of course operating condensing. Again, since in a Brewery, a great deal of steam is required for cooking purposes, the Engines may be so designed as to use the higher pressure of steam for doing work in a high pressure cylinder, exhausting at a pressure of 20 pounds into a receiver, from which all steam for cooking and heating purposes is drawn and then using the balance in a low pressure cylinder operating condensing.

In this way, the greater part of the expansive force of the steam has been made to do useful work, while it still contains its greatest part of heat, sufficient for all heating and cooking purposes.

The question of whether Oil or Gas Engine should be employed to drive Refrigerating machinery, must in all cases be decided by local conditions. As for example:—

If coal is worth \$3.50 per ton, and oil is worth 5c per gallon, leaving out all other questions but the fuel, the cost of a Horse Power per hour would be for a steam engine using 4 pounds of coal per hour per Horse Power:—

$$\begin{array}{r} 3.50 \\ \hline 2240 \\ \hline = 0.11c \times 4 = 0.44c \end{array}$$

For an improved compound Condensing Engine using only 2 pounds of coal per hour per Horse Power = $0.11c \times 2 = 0.22c$ and for an Oil Engine using 0.08 Gallon per hour per Horse Power = $0.08c \times 5 = 0.4c$.

Not considering the investment, which is slightly in favor of the steam engine, it can easily be seen that it would not be profitable to install Oil Engines in localities where coal may be had for a Dollar a Ton, while the price of Oil is 5c per gallon, nor would it be profitable to use Steam Engines where the price of coal is \$8.00 per ton and oil one Cent per Gallon.

Now, as to the installation of the Refrigerating Apparatus, after having selected the most suitable for our purpose, it will be necessary to pay the closest attention to its proper installation. The best machinery imperfectly installed will cause endless trouble and losses.

Pipe work in cellars must be properly proportioned to give the desired temperature.

Arrangements should be made for melting off the Ice whenever it reaches a certain thickness, as the heavy coating of ice on the pipes will reduce the efficiency of the cooling surface and consequently interfere with the temperature of the cellars.

Facilities for quick repairs to all parts of the system should be provided, as in most cases repairs are neglected on account of the difficulties attached to opening an ammonia system.

The property of wet surfaces or liquid having greater heat conduction, than dry surface or gas is being used to a great extent in systems of heat absorbing pipes under the name of flooded system. This system means that the pipes are entirely filled with liquid ammonia instead of part liquid and gas as in the ordinary way. Now, while this system has its advantages by adding about 20% to 30% to the cooling surface of the pipes, it has also the great disadvantage of sending liquid ammonia to the compressors, causing leakage in piston rods and damage to piston and cylinder, unless proper provision is made to return the unused liquid to the expansion pipes.

Now, as to the care and operation of the Refrigerating System, unless it is placed in the hands of competent and reliable men the best machinery will soon go to ruin. It is surprising to see the indifference on the part of some owners, as to who they put in charge of their refrigerating machinery, considering the amount at stake. In many instances the men in charge have not the slightest theoretical knowledge, the result is inefficiency of operation, with now and then loss of life.

To eliminate the danger to life, which is connected with the use of Ammonia, many attempts have been made to substitute other cold producing media, principally Carbon Dioxide, which is so plentiful in Breweries, but on account of the high pressure necessary to liquify this gas it has proven successful in a few cases only, where a ready market for liquid CO₂ is near by.

In conclusion it may be said that the only radical change in Brewery Refrigeration which may be looked for in the near future will be in connection with the changes of Brewery construction and the storage of Beer, as in the Duerkopp System, which is now being tried by the Pabst Brewing Co. Although some improvements have been made in refrigerating machinery, they have been of the general kind.

STUDIEN ÜBER DEN BROTEIG: ZÄHIGKEITSMESSUNGEN

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Obschon in jüngster Zeit die Arbeiten über den ursachlichen Zusammenhang der Mehlbeschaffenheit und Backfähigkeit wieder lebhafter aufgenommen sind, kann man nicht sagen, dass diese wichtige Frage eine *grundlegende* Förderung erfahren hat. Wohl sind über die Beeinflussung der Backfähigkeit durch Hilfsmittel der verschiedensten Art bemerkenswerte Resultate erzielt; auch ist der Einfluss der Backtechnik auf die Backresultate z. B. in Deutschland wesentlich geklärt worden, aber die Grundlage des Problems befindet sich nach wie vor auf dem toten Punkt labiler Beziehungen, die jeder Gesetzmässigkeit entbehren. Wie ich meine, aus dem natürlichen Grunde, dass die im Backresultat ausgedrückte "Backfähigkeit" eines Mehles viel zu viele und zu verschiedenartige Ursachen hat, um ihre bisher vergeblich gesuchte *unmittelbare* Bestimmung überhaupt zu ermöglichen.

Wir haben daher schon seit längerer Zeit in den Vordergrund unserer Arbeiten solche Untersuchungen gestellt, die das Verhalten eines Mehles in den *einzelnen Phasen* des Brotbereitungsprozesses beleuchten sollen und die Erfahrung lehrt, dass die Versuchsergebnisse hier auch eine *viel eindeutigere* Antwort geben als bei der direkten Frage nach der "Backfähigkeit."

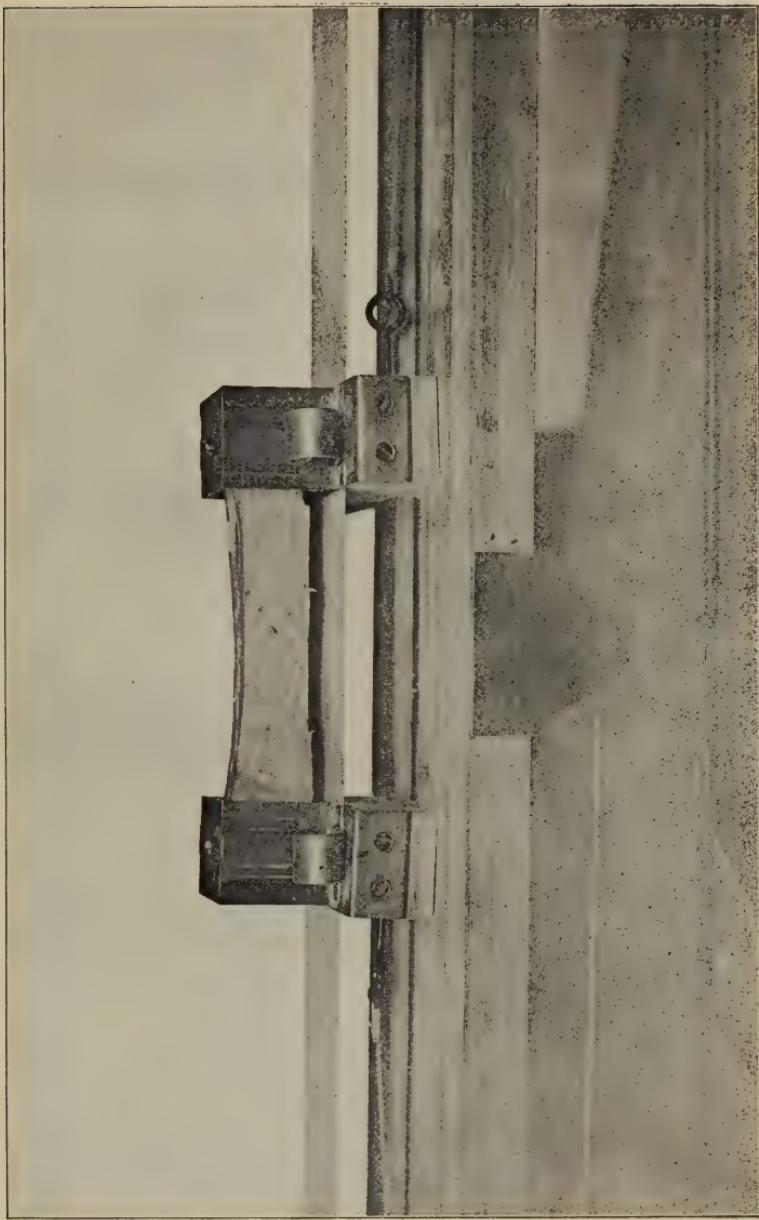
Die vorliegenden Versuche behandeln die dem Praktiker wohl bekannte Eigenschaft der verschiedenen Mehle, Teige von grösserer oder geringerer Zähigkeit zu geben. Als ein typisch "zäher" Teig ist ganz allgemein der Weizenmehlteig zu bezeichnen, der Roggenmehlteig dagegen weist eine ähnliche Zähigkeit gewöhnlich nicht auf, er arbeitet sich "kurz," wie es in der Praxis heisst. Nun finden sich aber sowohl beim Weizenmehl sehr zähe, normale und kurze Teige, wie auch beim Roggenmehl,

obschon die Bezeichnungen bei diesen verschiedenen Getreidemehlen nicht ganz das gleiche bedeuten. Was den Weizenmehlteig anbetrifft, über den hier zunächst nur berichtet werden soll, so ist eine normale Zähigkeit die für seine Aufarbeitung erwünschte Eigenschaft; wogegen Abweichungen nach dieser oder jener Richtung stets Schwierigkeiten mit sich bringen.

Die Beurteilung der Teigbeschaffenheit nach diesem Gesichtspunkt war bisher dem Empfinden, dem Griff des Bäckers überlassen und für die tägliche Praxis der Brotbereitung wird ja die Erfahrung des Bäckers auch in Zukunft das wichtigste Beurteilungsmoment sein und bleiben, anders bei der Versuchstätigkeit. Hier machte sich die Unsicherheit des Urteils über die grössere oder geringere Zähigkeit des Teiges für die Schlusserfolgungen sehr unvorteilhaft fühlbar und wir mussten daher versuchen, diese wichtige Teigeigenschaft zahlenmässig zu fassen.

In meinem Institut hat Herr Mohs nach verschiedenen vergeblichen Versuchen den hier abgebildeten Apparat konstruiert, der eine Messung der Teigzähigkeit, ausgedrückt in der Ausdehnungsfähigkeit des Teiges bei gleichmässigem Zug, recht gut zulässt.

Der Apparat zur Bestimmung der Teigzähigkeit besteht aus einer $1\frac{1}{2}$ m langen und 15 cm breiten Gleitbahn, die an beiden Enden auf 25 cm hohen Seitenwänden ruht. Auf dieser Gleitschiene können zwei Kufen, deren Gang durch Nutenführung bestimmt ist, von der Mitte her nach aussen bewegt werden. Die Bewegung der Gleitkufen von einander fort wird durch Drehen einer Rolle bewirkt, die sich unterhalb der Gleitschiene in der Mitte befindet. Beim Drehen der Rollenkurbel wickeln sich zwei dünne Seilkordeln auf der Rolle gleichzeitig entgegen gesetzt auf. Die Kordeln führen unterhalb der Gleitbahn nach den Seitenwänden, durch diese über Räder geleitet hindurch, und sind mittels beweglicher Schrauben an den Kufen befestigt. Durch Drehen der Schrauben können die Seile nach Bedarf gespannt werden. Ueber die obere Plattform der Kufen hinweg führt ein eingemehltes, breites, straff gespanntes Leinenband, das an den Seitenwänden befestigt ist, so dass die Kufen bei ihrer Bewegung unter dem Bande hinwieggleiten. Auf jede Kufe, das Band umfassend, so dass dieses durch einen Schlitz ungehindert



hindurchläuft, ist ein Metallrechteckwinkel aufgesetzt, aus dessen unterer Platte, die der Kufenoberfläche entspricht, fünf dünne Metallstäbchen senkrecht hervorragen. Die andere Fläche des Winkels erhebt sich am äusseren Rande der Kufe und dient als Führungsschiene eines Aufsatzkastens. In der Ruhelage stellen die Oberflächen beider zusammenstehender Gleitkufen ein nach oben offenes Kastengestell dar, aus dessen Grundfläche zehn runde dünne Metallstäbchen hervorstehen. In das Kastengestell hineinpassend kann ein Kasten aufgesetzt werden. Dieser Kasten besteht aus zwei gleichen oben offenen Teilen, die mittels eines Doppelwinkeleisens, das in Oesen an beiden Seiten des Kastens eingreift, zusammengehalten werden. Die Seitenwände des Kasten sind geriffelt. Beim Herausziehen dieses Doppelwinkels teilt sich der Kasten in seine beiden Hälften.

Bei der Ausführung eines Versuches werden 200 g eines Teiges in den zusammengesetzten zweiteiligen Kasten gelegt und dieser in das Kastengestell der Kufen hineingepresst, wobei die Metallstäbchen in den Teig eindringen. In der Mitte der Oberfläche beider Kastenteile befinden sich Löcher, aus denen die Luft entweichen kann und in die das mittelste etwas längere Metallstäbchen hineinpasst, so dass ein späteres Kippen der Kastenhälften verhindert wird. Nun wird das Doppelwinkel-eisen, das den Kasten zusammenhält, herausgezogen und beide Hälften ruhen auf den zusammenstehenden Kufen. Der Teig wird gehalten durch die hineinragenden Metallstäbchen, die Riffelung der Wände und die Adhäsion der Wandflächen. Beim Drehen der Rollenkurbel werden beide Kufen nach aussen bewegt und ziehen das Teigstück auseinander. Auf der Gleitbahn ist eine Centimeter-Teilung befestigt, auf der die Entfernung, bei welcher der Teig reisst, abgelesen wird.

Welcher Art sind nun die Fragen, die wir mit Hilfe dieser Messungen beantworten wollen?

Zunächst lag es nahe, zu versuchen, den Grad der Zähigkeit eines Mehles mit seinem Allgemeinverhalten in Beziehung zu bringen. Es wurden Messungen an Mehlen verschiedener Herkunft vorgenommen, wobei der Teig nur aus Mehl und Wasser angesetzt wurde. Das Ergebnis der Bestimmungen an den gerade zur Verfügung stehenden Mehlen war folgendes:

| | sofort | nach Studen | | | | | Mittel |
|-------------------------------------|--------|---------------|------|----------------|------|------|--------|
| | | $\frac{1}{2}$ | 1 | $1\frac{1}{2}$ | 2 | 3 | |
| | | | | | | | |
| Märkischer Weizen (Mehl 0-70)..... | 7,5 | 9,5 | 11,0 | 13,5 | 16,0 | 17,0 | 13,2 |
| derselbe (Mehl 0-10)..... | 9,0 | 11,0 | 13,0 | 14,5 | 16,0 | 16,0 | 13,3 |
| Square head..... | 10,0 | 15,0 | 16,0 | 16,0 | 17,0 | 18,0 | 15,3 |
| Elsässer Landweizen..... | 11,0 | 10,0 | 10,0 | 12,0 | 11,0 | 14,0 | 11,3 |
| Schwed. Perl Sommer (Märkisch)..... | 25,0 | 44,0 | 36,0 | 40,0 | ... | ... | 36,2 |
| Samara..... | 6,0 | 7,5 | 7,0 | 8,0 | 11,0 | 12,0 | 8,6 |
| Austral..... | 5,0 | 7,0 | 8,5 | 8,0 | 9,5 | 9,5 | 7,9 |
| Ulka..... | 9,0 | 10,0 | 11,5 | 9,0 | 12,0 | 12,0 | 10,6 |
| Wallachischer..... | 7,0 | 10,0 | 11,0 | 10,0 | 11,0 | 11,5 | 10,1 |

Die Zahlen zeigen, dass zwischen den einzelnen Mehlen bemerkenswerte Unterschiede hinsichtlich ihrer Zähigkeit auftreten. Es scheint, dass die einheimischen Weizen Mehle von grösserer Zähigkeit liefern, als die in Vergleich gestellten Sorten fremder Herkunft. Auch standen die erhaltenen Werte durchaus im Einklang mit der bei der Verarbeitung der Teige in dem Betrieb gemachten Beobachtungen. Doch möchten wir von Schlussfolgerungen allgemeiner Natur zunächst absehen und es einem grösseren Versuchsmaterial vorbehalten, zu erweisen, welche allgemeine Bedeutung den zahlenmässigen Zähigkeitsangaben zukommt.

Wichtiger war zunächst festzustellen, ob die Bestimmungsmethode geeignet wäre, unter gewissen Einflüssen erfolgende Zähigkeitsänderungen der Teige nachzuweisen.

Es wurde zunächst der Einfluss der Gärung geprüft. Dass die Zähigkeit eines Mehles unter der Einwirkung kräftiger Hefegärung abnimmt, ist erwiesen. Wir fanden als ganz allgemein gültigen Satz: *Je zäher das Mehl ist, desto kräftiger und flotter muss die Gärung gehalten werden.*

Sehen wir zu, in welcher Weise die Zähigkeitsmessungen den Einfluss der Gärung zum Ausdruck bringen:

| | Samara | Austral | Ulka | Square head | Perl Sommer | Märkischer | | Elsässer |
|-------------------------|--------|---------|------|-------------|-------------|------------|------|----------|
| | | | | | | 0-70 | 0-10 | |
| Teig Mehl + Wasser..... | 8,6 | 7,9 | 10,6 | 15,3 | 36,1 | 13,3 | 13,2 | 11,3 |
| " + Hefe..... | 8,3 | 5,7 | 8,7 | 9,4 | 26,5 | 10,3 | 9,3 | 10,6 |

Ganz deutlich können wir also mittels dieser Methode die Abnahme der Zähigkeit eines Teiges durch die Gärung nachweisen.

Erweisen liess sich ferner die mit der Dauer und Intensität der Gärung vermehrte Zähigkeitsabnahme der Weizenteige.

Bei dem erwähnten Perl-Sommer-Weizen betrug die Zähigkeit des Teiges aus Mehl und Wasser 26,2, bei Zusatz von Hefe 26,5, bei Teig der mittels vierstündigem Vorteig bereit war 22,0. Mit dem Fortschreiten der Gärung, mit dem Alter der Teige nimmt also ihre Zähigkeit ab.

Es konnte ferner gezeigt werden, dass die Zähigkeit bei weicheren Teigen grösser ist als bei festen Teigen, wie nachfolgende Zahlen für den Perl-Sommer-Weizen erweisen:

| | fest 160 | normal 164 | weich 168 | Aus- beute |
|----------------------|-------------|---------------|--------------|---------------|
| Teig: Mehl + Wasser. | 18,3 | 26,5 | 30,1 | |
| " " + " + Hefe. | 14,0 | 15,5 | 16,7 | |

Ist die Methode somit geeignet, Zähigkeitsänderungen eines Teiges, die theoretisch zu erwarten und praktisch nachweisbar sind, zahlenmässig auszudrücken, so dürfte sie sich auch, wie wir erwarten, für die Festlegung absoluter Zähigkeitswerte brauchbar erweisen. Doch ist hierfür ein umfangreicheres Versuchsmaterial nötig, um festzustellen, in welchem Masse die Zähigkeit mit Herkunft, Sorte und Allgemeinverhalten der Weizen veränderlich ist.

THE APPLICATION OF TAKA-KOJI IN DISTILLERIES

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On account of the often great variations in the price of barley malt (in two consecutive years the price varied 100%), it would be of great value to the distilling industry if a converting medium of moderate and more uniform price could be employed instead of barley malt. Malt made from other kinds of grain would have the same objection attached to it as malt from barley, namely the variation in the price of the raw grain. Furthermore, experience has shown that the diastatic power of malt, produced from the several other kinds of grain, has been inferior to that of barley malt.

Eliminating therefore the different grains as a source of converting medium, I turned to the diastase produced by a micro-organism, the *Aspergillus Oryzæ*.

It is not a new idea to employ the diastase produced by the *Aspergillus Oryzæ* in the formulating industry. On the contrary, this fungus has been used in East Asia from time immemorial in the manufacture of Saké or rice beer, the national drink of the Japanese. "Koji" is the name applied to rice grains which are grown over and penetrated by the mycelium of *Aspergillus Oryzæ*. The preparation of the "Koji" is as follows: the rice grains are steamed and the conidia of the fungus, a yellow green powder, called "tane koji," is sown on them. The germination then takes place, the temperature being held at 20 to 25 degrees C. It is claimed that one volume of conidia is sufficient to turn about 40000 volumes of rice into Koji.

A Japanese, Dr. Jokichi Takamine, was the first to introduce the Koji process in America. As far back as 1889 he advocated the use of Koji in the distilling industry, and through his efforts a company was formed to try the idea out on a large scale. Instead of growing the fungus on rice, Takamine employed a

material far cheaper for this country, namely wheat bran. He patented his improved method of growing the fungus and also his method of extracting the diastase.

Lafar (*Handbuch der Technischen Mykologie*, Volume 5, Page 331) describes the "Takamine process" as it was carried out by Takamine himself during his experiments on a large scale in Peoria, Illinois, about twenty years ago. An extract of the wheat bran on which the *Aspergillus Oryzae* had been allowed to germinate, contained the diastase, produced by the *Aspergillus*, and this extract was mixed with the mashed grain, bringing about the conversion of the starchy materials. A Japanese yeast was used to ferment the sugar. The account states that a yield of between 2.5 and 5% in excess of that ordinarily gotten was obtained. In spite of this fact, however, the distillery was closed down after a couple of years.

Since then, as far as my knowledge goes, no other experiment has been made in this country to employ the diastase from Koji as a converting agent for distillery mashes. While Takamine abandoned his process in Peoria, several patents in later years have shown that he from time to time has been improving his method of manufacturing his Taka-Koji, as the Koji from his special process is called ("Taka" means "High" in Japanese. "High in diastase"). Lately, I understand, he has succeeded in adapting a modification of the Galland-Henning malt drum system to his process. This should be a great improvement over the old floor system, in so far as it makes it possible to work under absolutely sterile conditions.

By courtesy of the firm of Parke, Davis & Co., Detroit, Mich. which firm is manufacturing Taka-diastase for medicinal purposes after the Takamine process, I was fortunate to procure for my experiments whatever amount I wanted of Taka-Koji, which had been manufactured by the latest improved method.

For my experiments I decided to use the Taka-Koji itself instead of the diastatic extraction of same and add it to the mash in the same way as malt. The purpose was to save the expense of extraction and also to add to the mash all the valuable nitrogenous substances contained in the Koji. I also decided to use the same species of *Saccharomyces cerevisiae* as

was used in our ordinary mashes, instead of the special Japanese yeast which had been employed previously.

At the time of the experiments I did not intend to publish my results. If I had, my observations would have been more comprehensive. If therefore something is lacking in completeness, an excuse might be found in this statement.

Before beginning the practical experiments in the distillery, laboratory experiments were conducted on a small scale to ascertain the amount of Taka-Koji which was necessary to convert a certain amount of starch into sugar, and also the optimum temperature to conduct the conversion at.

It was found that 4 g. of Taka-Koji was sufficient to give a complete conversion in a mash made from 96 g. of corn and rye, the corn containing 15.0% of moisture, and the rye 14.0%.

The best temperature for converting was found to be between 50 and 55 degrees C. By increased temperatures a gradual decrease in the converting power was found.

Three experiments were made in the distillery.

For the first experiment only a 14 gallon can was used and a portion of our ordinary mash from the mashtub was employed, the mash being taken from the main mash just before malt was going to be added for conversion. The Taka-Koji was added in air dry condition, the amount being 400 g., an amount that corresponds to 4% of the combined weight of Koji and grain in the portion of mash used. The mash was left at 55 degrees C. for 20 minutes when it showed complete conversion. It was then cooled rapidly, water added to bring the sugar solution to a strength of approximately 9.5 Balling (specific gravity: 1.0384) and ordinary yeast added in the same proportion as used in the large fermenting tuns. The can was suspended in a fermenting tun which had been filled the same day. The object of this was to be able to maintain proper temperatures during the fermentation.

48 hours after the can was pitched, the fermenting mash showed a specific gravity of 0.9998 and an acidity of 4.5 (4.5 cc. 1/1 N NaOH to 100 cc. of mash). The large fermenting tun which was pitched the same day as the can showed after 48 hours a specific gravity of 1.0058. After 67 hours the specific

gravity of the mash in the can was 0.9984, acidity 5.5. This was the logical end point. From now on the acidity increased rapidly.

The fermenting mash tasted very bitter on the second day of fermentation but at the end of the fermentation, the taste was about normal. A black scum had formed on top of the fermenting liquid. It stayed on to the last. It might possibly be traced to the fact that the Taka-Koji was a trifle overgrown.

The second experiment was performed on a somewhat larger scale. Instead of using mash material from the mashtub, the mash was made separately. It consisted of 500 Kg. altogether of which the 20 Kg. were Taka-Koji. The fermentation showed the same peculiarities as in the former experiment, namely the rapid fermentation and the bitter taste during the first half of the fermentation.

In these two experiments it was not possible to distil the fermented mashes in a practical way so as to ascertain the quality of the spirit. The amount was too small for the regular stills.

The third experiment was performed on a good sized working scale. Two mashes, each consisting of 3401.94 Kg. (of which 131.5 Kg. was Taka-Koji) were prepared as follows: 22.7 Kg. of Taka-Koji was introduced into the mashing water (temperature 55 degrees C.) together with the finely ground corn and brought to a temperature of 88 degrees C., where it was left for some minutes. It was then cooled to 70 degrees C. at which temperature the rye was introduced. It was further cooled to 55 degrees C., when the balance of Taka-Koji, 108.8 Kg., was added. The mash was held at this temperature until fully converted and then cooled down in the mashtub. Before running the mash out, water was introduced to bring the specific gravity to approximately 1.0384 (9.5 Balling). At the temperature of 20.5 degrees C. the mash was let out of the mashtub, mixed with the yeast and run to the fermenting tun. The mashes showed complete conversion 15 to 20 minutes after the Taka-Koji was introduced.

The two mashes were filled in tun No. 25 on Friday, May the 26th, 1911. On Saturday at 9 a.m., the temperature had gone

up to 29 degrees C., a remarkably quick rise; at this hour the specific gravity was 1.0220 and acidity 4.0 (4 cc. of 1/1 N NaOH per 100 cc.) On Sunday the temperature had risen to 34 degrees C., while the specific gravity had fallen to 1.0004 and the acidity increased with 1 cc. The highest temperature, 34.5 degrees C., was reached early Monday morning. At 9 a.m. it was again 34 degrees C., the specific gravity 0.9988, acidity 5.5. At 3 p.m. specific gravity 0.9980, acidity 6.5. This was the logical end point for at 5.30 p.m. the specific gravity had increased to 0.9984 and the acidity to 7.0. The fermented mash was therefore run to the still at once.

To better realize the quickness of the fermentation, it is only necessary to compare Tun No. 25 with Tun No. 52, another tun of the same size. Tun 52 was filled some hours before Tun 25 with two mashes which were identically the same as the two mashes in Tun 25 with the one exception that barley malt was used as converting agent instead of Taka-Koji. Although Tun 52 was filled before 25 and started at the same temperature of 20.5 degrees C., nevertheless the temperature had only risen 25 degrees C. on Saturday against 29 degrees C. in Tun 25. On Sunday Tun 52 registered 30 degrees C. against 34 degrees C. in Tun 25, and while Tun 25 was ready to go to the still at 3 p.m. on Monday, Tun 52 did not finish fermentation before late Tuesday night and was not distilled before Wednesday morning.

In the fermentation of the Taka-Koji mashes there was practically no so called after-fermentation. The fermentation was ended when the maximum temperature was reached. While this is distinctly different from what we else consider a normal fermentation, I count it a great advantage. It is always during the afterfermentation that the yeast gets weak, a circumstance which gives the injurious bacteria an opportunity to thrive and cause an excess of acid.

Like in the previous experiments, the fermenting mash was characterized with a bitter taste. It also gave off a sharp, disagreeable odor which adhered to the spirit after distillation, although in a somewhat smaller degree. The taste of the spirit was somewhat similar to what we designate as a musty taste. By redistillation through a column still, however, but without fil-

tration through charcoal filters, both the disagreeable odor and taste disappeared, leaving a spirit, pure in smell and taste.

Tun No. 25 was distilled separately and the yield was 36 Liter of 100% Alcohol per 100 Kg. of mash material, just a trifle higher than the yield of the other mashes which were made the same day. If we take in consideration the fact that the fermentable extract from the wheat bran is considerably smaller than the extract from the barley malt, the comparative yield from the grain proper is still higher.

As previously stated, the spirit was, after the second distillation, pure in taste and odor. It has happened, however, that a spirit, which tasted and smelled normal after distillation, has developed an abnormal odor and taste after it had been kept in storage for some time. For instance, this has been the case with some spirit which was distilled from cane sugar molasses. The spirit was normal in taste and flavor after distillation but in course of time it developed a very characteristic rum taste.

To give the spirit from the Taka-Koji process every chance, a barrel of the reduced spirit from the second distillation was warehoused. The spirit was reduced with distilled water to 45% alcohol and put in an old charred barrel and stored in a warehouse which was heated artificially during the cold season. The spirit has developed normally and no abnormal taste or odor can be detected. As an abnormality would surely have shown itself by now, it may be safe to say that the spirit is normal and will continue so.

In judging the adaptability of Taka-Koji for use in distilleries several questions must be asked and answered.

Is Taka-Koji capable of giving a complete conversion of the starchy materials in the mash?

Yes, 4% of the air dried Taka-Koji will in 15 to 20 minutes give a complete conversion of well prepared mash material.

Is not the temperature of 50 to 55 degrees Centigrade too low to assure the sterilization of the mash?

No. While malt may contain injurious bacteria and the mash converted with malt at as low a temperature should be heated to 66 to 67 degrees C. to insure its sterility, the Taka-Koji may be prepared from sterilized material by a pure culture

under sterile conditions, and therefore no sterilization should be necessary in the mashtub.

Is the fermentation a satisfactory one?

While it is accompanied by a strong odor, which is prevalent in the fermenting room, the fermentation, however, is very rapid and complete, and on this account should give rise to the least amount of infection.

Is the yield of spirit satisfactory?

Yes, the yield obtained was a little higher than the yield gotten from the barley malt mashes, although the total fermentable extract, available in the mash material, was less. The yield of 36 Liter of 100% Alcohol per 100 Kg. of mash material is of course only a comparative yield. In distilleries which employ cookers and boil the corn under pressure, a higher yield would naturally result.

Is the spirit from the first distillation normal and would it be possible to use this spirit for potable spirit?

No. The spirit from the first distillation has a kind of musty taste which would prevent its use for potable spirit. The use of Taka-Koji for the manufacture of unrefined whisky could therefore not be recommended.

How is it made potable?

By redistillation in column still, but without filtration through charcoal filters, it loses the abnormal taste and becomes pure and sweet.

What would be the comparative cost of Taka-Koji and barley malt?

The Taka-Koji is made from wheat bran which material is cheaper than barley at its lowest price. The process of making Taka-Koji is more scientific than the malting of barley. It needs more competent men and in this feature is more costly. On the other hand, the process is of shorter duration, and therefore a comparative smaller plant is needed. Taking everything into consideration I think that the Taka-Koji should be bought for between 4 and 5 cents per Kilogram. This price would correspond to a rather low barley malt price. And then it must be remembered that 4% of Taka-Koji is all that is needed, while

the amount of malt employed in many places is twice this or even more.

Therefore I should say as a final conclusion that in distilleries which make commercial or potable neutral spirit, the Taka-Koji process could be introduced to advantage. Besides from a probable higher yield in spirit, the saving in malt cost would be worth while in years with normal malt prices and very considerable in years when the malt prices become abnormal.

THE QUALITATIVE REGULATION OF THE EXTRACT OF BEER-WORT AND BEER IN BREWERY PRACTICE

CARL RACH,
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The Beer production in all countries of the world is steadily increasing and amounted during the last year to approximately 250,000,000 barrels. The consumption of beer in the United States of America has practically doubled within the last 20 years. In England, Germany, Austria, France and Belgium, it is steadily rising. If we figure approximately 50 lbs. of malt or malt and unmalted cereal and $\frac{1}{2}$ lb. of hops per barrel of beer, the production of 250,000,000 barrels of beer for the world's use would require 12,500,000,000 pounds of starchy brewing material and 125,000,000 pounds of hops. This vast amount of raw material must be produced by agriculture. It keeps the farmer continually busy and brings him the corresponding financial returns. The brewing industry occupies an eminent place among the industries of the civilized countries and a great number of allied industries are employed by it in the most profitable manner. The manufacture of beer creates means of existence for a whole army of men. These conditions clearly define the position of the brewing industry from the standpoint of political economy. The brewing of beer is of the greatest advantage however to the individual, giving him a healthy, pure, palatable, refreshing and nutritive food beverage. No other product is of such uniform and unvarying quality, and this explains its popularity. A glass of beer and a piece of bread, although very modest, represent a meal which satisfies both hunger and thirst.

The brewing industry produces two great types of beer, one by "top" and the other by "bottom" fermentation, according to the kind of yeast employed and the temperatures maintained. Types of top-fermented beers are English and American ale,

stout, and porter, Belgian beer, German and Danish top-fermented beer, Weiss beer, Australian beer, etc. About one third of all the beer produced is "top" and two thirds "bottom" fermented. The main types of "bottom" fermented beers are the following: Bavarian beers, (Munich, Nurnberg, Erlangen, Kitzingen), Bohemian beers, (Pilsen), Austrian beer (Vienna), Dortmund beer, Carlsberg beer (Copenhagen), and Strasburg beer, Lager beer of the United States, etc. England, its colonies and Belgium mostly consume "top" fermented beers, whereas Germany, Austria, France, Switzerland, and the United States are the principal consumers of "bottom" fermented beers.

Beer is made from hopped beer-wort produced by the mashing and brewing processes. The average quantity of raw material employed for the production of a barrel of hopped beer-wort containing from 32 to 35 lbs. extract is approximately 50 lbs. made up of malt or malt and unmalted cereals and $\frac{1}{2}$ lb. of hops. The main qualities of the beer-wort necessarily depend upon the kind and quality of the raw materials and the method of brewing them. It is a fact that in all countries where large amounts of beer are consumed, as for instance in Bavaria, the quantity of hops used per barrel, or hecto-liter of beer, is comparatively small. The quality of hops naturally varies and it may be said of the best varieties that they are to beer what spices are to other foods. Strongly hopped beers are not regarded with much favor. One hundred parts by weight of hops do not impart to the beer-wort any more than twenty parts by weight of extract; the amount of hop extractives in the finished beer may therefore be regulated by the amount and quality of hops added. The analytical results show that those types of hops known as "choice" (edel) contain less hop-oil, less hop resin, less hop bitter acids and tannic acids than the common types. Therefore beer produced from the use of "choice" hops contains less hop extractives than beer brewed with common hops.

Much more important than the hop extractives are those constituents of the beer-wort and beer which are derived from malt or malt and unmalted cereals by the mashing and brewing processes. Let us study at 12° B. wort, containing $32\frac{1}{2}$ lbs. of extract by weight in one barrel. Its chemical composition must be of

the greatest interest to the practical brewer because it determines the taste, the palate-fulness, the alcohol content, foam keeping quality, color, brilliancy, etc. of the finished beer. The extract may contain various ratios of sugar to non-sugar, sugar to dextrin and of sugar to the soluble nitrogenous constituents. The ratio of sugar to non-sugar in the wort determines the alcohol content of the finished beer, a fact of main importance. The production of beer has developed immensely with the introduction and use of steam in place of direct fire boiling. Before that time beer was produced in many small breweries and in the family copper. But the small breweries have been replaced in all countries by fewer and larger breweries producing many million barrels of beer annually.

As an article of consumption, as a food beverage of the masses, beer is recognized by the governments of all civilized countries and used by them as a source of revenue by high and strictly enforced taxation.

Looking over the tables of beer analyses for the last fifty years, we observe that the heavy gravity beers of old have been displaced by beers of lighter gravity, and that the percentage of alcohol has steadily decreased. Progress in modern chemistry and physiology has taught the brewer not to waste the valuable extractive food constituents of the beer-wort unnecessarily during the fermentation. During this process, the general rule prevails that two parts of malt sugar produce one part of alcohol and one part of carbonic acid gas. If a portion of the fermentable malt sugar is displaced by unfermentable extract, the formation of alcohol and carbonic acid is proportionately decreased. We necessarily require malt sugar in the beer-wort because without it there would be no fermentation and consequently no alcohol or carbonic acid gas, both of which are necessary and normal constituents of finished beer. There is a growing tendency among brewers to produce ordinary draught beers with not more than 3% of alcohol. This may be done by making 10% Balling wort, but is impossible, if worts of 12 B. or more are employed. How can we avoid lowering the extract in the wort if we must decrease the alcohol of the finished beer? If two parts of sugar produce one part of alcohol, we should have in a

12% wort no more than six parts of fermentable sugar, and must therefore either produce a wort containing this amount of malt sugar or if it be in excess, must have a means of eliminating it before fermentation. The principal prevailing methods employed in the brew house for the production of beer-wort are known as "decoction" and "infusion." Neither of them enables us to regulate the percentage composition of the wort in a manner required and desired despite the contrary assertions in several well known text books of brewing. The restriction of sugar production up to a certain degree may be successful with the "decoction" method, but only if very highly kilned malt and a very voluminous "lautermash" are employed, and if the diastatic action is interrupted and inhibited at the proper time while drawing off the wort. The formation of sugar during the "infusion" method can only be sufficiently restricted if a separation of thick and thin mash is accomplished after mashing in; if very high temperatures are employed during the mashing off; and the diastatic action is checked in time. The usual "decoction" and "infusion" methods with the ordinary brewing material do not therefore allow the required regulation of the sugar contents of the wort and a great many improvements may be made in this direction by careful and thorough investigation. I propose three new methods which may accomplish this result as follows:

1st: The conversion of the formed sugar in the wort extract into unfermentable products by means of caramelization. A large portion of the first wort is heated in a pressure kettle with 25 to 30 lbs. of pressure or exposed to a temperature of 105 to 110 R. This changes the malt sugar chemically into unfermentable wort extract. The caramelized wort is now added to the other wort in the kettle and boiled with hops as usual.

2nd: A large amount of the first wort is evaporated in vacuum pans to syrupy consistency. The separation of the malt sugar is accomplished in a special manner at this stage. The residual product is an extract poor in malt sugar which may be dissolved in water and added to the remainder of the wort in the kettle.

3rd: Concentrated beer worts poor in malt sugar or maltose

are produced; and these are used for krausening beers produced from worts low in malt sugar.

The methods described above are entirely new and much time will be required for perfecting them for practical use. Good results are expected from the tests made up to the present for regulating the ratio of the sugar to non-sugar in the wort and the alcohol content of beer. I have demonstrated in former publications by accurate figures the large losses, especially in American breweries, resulting from the high percentage of fermentable sugar in worts and the unnecessary destruction of valuable extract during fermentation. It is equally difficult to regulate the ratio of the soluble protein to the remaining extract in the wort and beer. The latter is principally determined during the malting process. Worts and beers rich in peptones can only be produced from fully grown malts, carefully handled on the floor and kiln. The assistance of the peptase is of course much desired during the mashing process, but it is present in only very limited quantities. The action of the peptase is much more energetic during the growth of the barley on the floor and the soluble albuminoids for the wort and beer are produced during that period. Two processes remove from the beer the coagulable and the soluble protein—the boiling of the wort and the activity of the yeast. A large percentage of coagulable albuminoids and all the valuable and useful enzymes of malt are eliminated during the boiling process and naturally lost to the finished beer. The protein not removed during the boiling process, is to a large extent, assimilated by the yeast and the resulting beer is low in albuminoids. In order to avoid the great loss of protein I have proposed, for the production of draught beer, to concentrate a portion of the first unboiled wort in a vacuum pan at a very low temperature, not above 40 R. After cooling and filtering, this wort is kept in the storage cellar and added to the beer at the time of racking. I have also tried to treat the last worts of lower gravity as regular beer-worts and to use the first worts of heavier gravity for krausening purposes and vacuum concentrations in order to be able to produce beers with high protein content and high nutritive value.

The tendency to produce highly fermented, stable, and bril-

liant beers is an obstacle to the manufacture of nutritive beers. There is nothing easier and simpler in practical brewing than the production of worts of 12 B. with a high sugar content and with an attenuation of 70 to 80 % in the cellar. Beers are most profitably made from such worts and are well suited for export.

There seems to be a strenuous effort on the part of the brewer to produce the largest possible quantity of finished beer in the shortest possible time and thus distribute the expense for brewing operations over the largest quantity of beer possible. Large brewing outfits are fast becoming a necessity and brew-house capacities of 500 to 600 barrels at a brew are common in the United States. It is only a question of time when we shall have the thousand barrel at a brew outfit. The manufacture of these enormous quantities of beer naturally develops the mechanical and technological part of the brewing industry more rapidly than the chemical. Chemistry of brewing is pushed to the background. But it is of the greatest importance to preserve the nutritive qualities of beer and if at all possible, to increase them. Chemical and physiological facts as well as the prohibition movement ought to stimulate the production of beers low in alcohol and rich in extractive substances. If the brewing industry is blind to the recognition of these facts, other industries will spring up for the purpose of resolving them. It is very probable that the brewing industry of the future will develop in two distinct ways:

1st: The production of beer on a gigantic scale in comparatively few breweries, with enormous development of trade, technology and intricate machinery.

2nd: The chemical technology of brewing will be rejuvenated; the originality of the beer brewer revived; and beers of a new and peculiar character and of greater nutritive value will come into favor.

Beer of good quality and moderate cost, beer as a food beverage for the great masses of civilized countries should ever be the watchword of our great brewing industry.

(*Abstract*)

RELATION OF THE REDUCING POWER TO THE
FERMENTATIVE CAPACITY OF VARIOUS
CARBOHYDRATES

EMIL SCHLICHTING

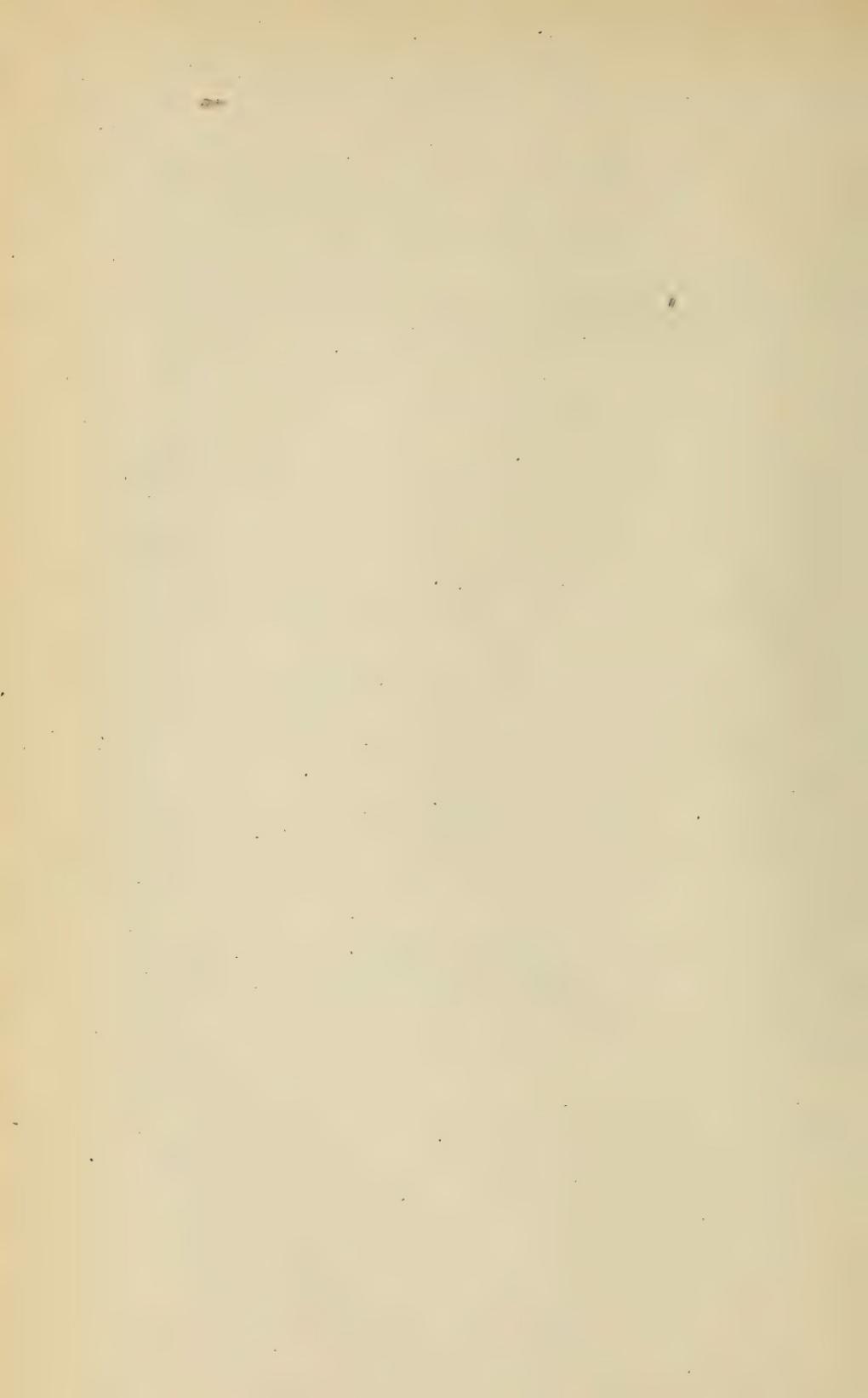
The paper recites a large number of experiments from which the author has drawn the following conclusions:

(1) All results found for the amount of actual fermentable sugars by the fermentation method are generally too low, and form about 1 to 6 per cent less than the real amount of sugars present, excepting in mixtures of equal parts of Saccharose and Dextrose.

(2) Fermentation methods of sugar determination should be invariably carried out with pure cultures of yeasts, under uniform conditions of time, temperature, nature and quantity of yeast nutrients.

(3) Certain real relations undoubtedly exist between the reducing power and the fermentability of sugars which enable the analyst to find the correct amount of fermentable sugars, especially when only two carbohydrates (of those mentioned) are present.

(4) When more than two sugars are present in the solution, the results found for fermentable sugars by their reducing power are from 3 to 6 per cent in excess of the truth.



(*Abstract*)

THE GROWTH AND DEVELOPMENT OF THE BOTTLING BEER INDUSTRY OF THE U. S.

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Based upon accurate figures gathered over a long period of practical experience in his own bottling beer plant, the author points out that in order to successfully and profitably conduct the bottling of beer in the brewery proper, the following rules must be observed:

1. A properly brewed beer from first class materials according to the most modern, scientific methods.
2. Modern up-to-date machinery for washing, rinsing, filling and pasteurizing operations.
3. Absolute control over losses of bottles by enforcing payment for bottles by consumers at the first sale.

Author states the itemized cost of bottling 1 barrel of beer as \$2.76 or \$0.23 per case.

THE PHOSPHATE DEPOSITS OF CONTINENTAL NORTH AMERICA

LUCIUS P. BROWN
Nashville, Tenn.

It seems hardly necessary in this Assembly to call attention to the importance to chemists of the industries based upon phosphate of lime. Suffice it to say that in the United States alone, the three largest concerns manufacturing fertilizers have an aggregate capital of some \$180,000,000. and the total American capital investment in this business is probably not far from \$300,000,000. The product in 1911 was about 6,000,000 tons of fertilizers, which, at an average price to the consumer of \$20.00 per ton, was worth about \$120,000,000. The average rate of increase in the consumption of fertilizers in the United States has for the past fifteen years been approximately ten per cent per annum, and since on a very small proportion of the farming area are fertilizers used, the opportunities for expansion are great, and no diminution in this rate of increase may be looked for, but the contrary rather. Moreover, a large part of the phosphate of lime production of the United States is shipped abroad.

It is, therefore, fortunate that the phosphate deposits of the Continent of North America are, since the discovery of the great beds of the Rocky Mountain states, unquestionably the largest now known. This paper will endeavor to give some description of them, gleaned mostly at first hand, and touching on their chemical and geologic aspects.

Phosphoric acid is so migratory a substance that no single theory as to derivation of a material containing it will answer for all known deposits, and this is almost equally true of any single deposit. Without doubt we ought to consider the primary rocks of the lithosphere (that is, the so-called igneous rocks) as the original source of the phosphoric acid of all the sedimentary rocks, and must not forget that these igneous rocks themselves

furnish a certain small proportion of the phosphate of commerce. It is interesting to note that Dr. F. W. Clarke calculates, as a result of unusually exhaustive work (for the details of which I must refer you to Bulletin 491, U. S. Geological Survey) that the ten mile deep lithosphere is composed of 95 per cent of igneous rock and five per cent of sedimentaries. The igneous rocks contain according to analyses quoted by Clarke, an average of .26% of phosphoric acid, the sedimentaries .18%. This difference, though slight, is sufficiently notable to mean something when the enormous total mass of the lithosphere is considered, and the deficiencies in the sedimentaries would lead us to expect that concentration which we in fact find in certain beds.

For all practical purposes we may consider that the phosphate of the crystalline rocks exists as apatite, the other crystalline phosphates being altogether subordinate. Its wide distribution, to be inferred from the data just given, is confirmed by geologists. Bischoff¹ has shown that phosphate of lime is comparatively soluble in carbonated water, and that other forms of calcium phosphate are much more so. Minssen and Täcke, according to Clarke,² have shown that its solubility is increased by humus acids, while C. L. Reese has shown that it dissolves perceptibly in swamp waters rich in organic matter, and that while it dissolves freely in carbonated waters, it is redeposited when the solution is allowed to stand over calcium carbonate. It is to be inferred from this that a ground-water containing phosphate in solution would deposit this phosphate when it comes into contact with a limestone. Other salts in solution hinder or assist the solubility of calcium phosphate. Bischoff³ notes that while it requires 5,432 parts of carbonated water to dissolve one part of calcium phosphate, it requires only 3,150 parts of such water containing about 8 per cent of common salt, and the presence of ammonium chlorid promotes solubility still more. Cameron and Hurst⁴ studying the solution of iron, aluminum and calcium phosphate, showed that the process is one of hydrolysis—the solution becom-

¹ Bischoff. Dict. of Chem. Géology.

² Loc. Cit.

³ Loc. Cit.

⁴ Jour. Amer. Chem. Soc. Vol. 26, p. 885.

ing acid and less soluble basic phosphates being left behind; that is, the solution contains acid ions, corresponding either to free acid or to acid salts, a condition which must materially affect the action of the liquid upon the substances with which it comes in contact. The great increase in solubility of carbon dioxid in water under pressure must further not be lost sight of, since the earth's circulating waters, even at moderate depths in the crust, must be under such pressure and where such water contains dissolved carbon dioxide its solvent action would probably be very greatly augmented.

Bearing in mind now the methods of solution, carriage, redeposition and concentration of phosphate of lime, we may profitably pass to a consideration, of the several phosphate deposits themselves.

A convenient if somewhat empiric classification of industrial phosphates is as follows:

| | | |
|--|--|----------------|
| A. Phosphates of definite mineral composition, or Mineral Phosphates | A-1. Apatites. | |
| | Canadian Deposits | |
| B. Phosphates of indefinite chemical composition, or Rock Phosphates | A-2. Wavellites. | Virginia Veins |
| | Mount Holly Springs, Pa. | Tennessee |
| B-1. Nodular Phosphates | B-1-1. Nodules in soft Matrix | |
| | Deposits of So. Carolina and Florida; "white Rock" of Tennessee, Minor deposits of Georgia, Alabama, Mississippi, etc. | |
| B-2. Stratified (See following page) Phosphates | Certain "Brown Rock" | |
| | Deposits of Tennessee. | |
| B-3. Phosphates apparently due to Terrestrial Animal life. | B-1-2. Nodules in hard matrix or conglomerates. | |
| | "Kidney Phosphates" of Tenn. and adjoining states. | |

| | | |
|---|---|---|
| B-2. Stratified Phosphates | B-2-1. Phosphatic Lime-stone beds. | B-2-1-1. Leached. ("Brown" Phosphates of Tennessee and Kentucky |
| | B-2-2. Pure but unleached stratified Beds | B-2-1-2 Unleached (Blue limestone, forming "mother Rock" of "Brown" beds. |
| | B-2-3. Impure but unleached Stratified Beds | B-2-2-1. "Blue Rock" of Tennessee |
| | | B-2-2-2. "Hard Rock" of Maury County, Tennessee. |
| | | B-2-2-3. Silurian Beds of Arkansas |
| B-3. Phosphates Apparently due to Terrestrial Animal Life | | B-2-2-4. Bedded Phosphates of the Rocky Mountain States |
| | | B-2-3-1. Impure "Blue Rock" of Tennessee |
| | | B-2-3-2. Devonian of Arkansas |
| | | B-2-3-3. Impure Bedded Phosphates of Rocky Mountain States |
| | | B-3-1. Soluble Guanos. (But Guanos, etc. Relatively unimportant) |
| | | B-3-2. Phosphates due to leaching or Decay of Guano Deposits. (No continental American Deposits) |

The crystalline apatites were naturally among the first phosphates mined for industrial use, not only in America but elsewhere. The Canadian deposits were first described by Dr. T. Sterry Hunt¹ in 1848, and mining operations were begun in 1871. They occur both in Quebec and in Ontario, in two belts, the longer diameter of which is approximately North and South.

¹ Bulletin 315 U. S. Geol. Sur.

The deposits occur almost without exception in veins and lenaes in association with pyroxenic and horn blendic rocks, the country rock, being largely quartz, and gneiss. A very noteworthy association is with mica and feldspar, particularly the former. The production was never very large, probably 25,000 tons in any one year at the outside. The quality was usually high, say from 75 to 85% phosphate of lime (so-called "Bone Phosphate"). With the development of the high grade deposits of Florida, mining of this material for export has practically ceased, and at present only a few thousand tons per annum is being mined for local consumption. The old phosphate mines are being worked chiefly for the mica they contain. The Canadian deposits are therefore, no longer of importance.

In Virginia apatite occurs in Nelson, Amherst, and adjoining Counties. The beds consist of apatite in grains and small crystals in a matrix of crystalline ilmenite (the oxid of Ti and Fe) which in one considerable deposit is replaced almost altogether by rutile (titanium oxide). The country rock is a strongly foliated Archean gneiss. The origin of the deposit is evidently igneous, and so close association of the minerals in such amounts is not known elsewhere, although they frequently accompany each other, as at Kragero in Norway. Because of difference in the magnetic permeability, that of the ilmenite being high while that of the apatite is low, the minerals can be separated magnetically, but owing to the distance from rail and the probable fairly high cost of this separation, these deposits are not at present being worked, and the probabilities are against their early development. In addition to this locality a certain small amount of apatite is obtained as a by-product in the mining of certain magnetic iron ores in the Archean rocks of Northern New York, but as will be inferred the production of apatite industrially in North America is practically negligible. So far as I know it has not been largely used for the manufacture of fertilizers, a certain amount going to the manufacture of phosphorus and phosphate baking powders, its purity recommending it highly for such purposes.

Wavelite (crystalline phosphate of alumina) is mined at only one point in the United States; namely Mt. Holly Springs Pennsylvania, twenty miles southwest of Harrisburg. G. W.

Stose¹ describes it as occurring in white clay, associated with manganese and iron ores. It appears to be a secondary deposit only, surface gravels, and sand clays covering the rock at the foot of South Mountain where it occurs. The deposits are in part residual and in part transported. The wavelite occur chiefly in nodular forms with radiate structure. Phosphorus was probably associated with the iron in its original occurrence, and in the process of redisposition combined with the alumina, but it is possible that it may have been in part derived from the phosphatic animal remains in the sediment, such phosphatic material being moderately abundant in the unaltered rocks, and having been removed from the upper beds altered or unaltered. This material is used altogether at this place for the manufacture of phosphorus. The deposit in Tennessee is of comparatively recent discovery, and so far as is known exists in a more or less impure form, corresponding somewhat to the deposits of phosphate of alumina of certain of the West Indian Islands, with the important difference that the phosphorus deposits of Tennessee have probably been derived by leaching from the surrounding phosphatic limestone (and not from "bird deposits") with subsequent redisposition in a shale or aluminous limestone.

Passing now to the much more important phosphates of indefinite chemical composition, or rock phosphates, we find these assuming a multitude of forms and illustrating well the protean aspect of phosphate of calcium, to which attention has been called by Shaler². The rock phosphates occur as nodules, as stratified beds forming a part of the stratification of the regions in which they occur, and as phosphates apparently due to terrestrial animal life.

Taking up first the nodular phosphates, these may be divided in general as nodules in soft and hard matrix, and are those which furnish much the larger part of the production in the United States. Taking up first the nodules in soft matrix, the South Carolina Deposits were first mined about 1867, and mining has since been continuous. The South Carolina phosphate district lies along the coast in the neighborhood of Charleston, in a belt

¹ Bul. 315 U. S. Geol. Sur.

² Bul. 46 U. S. Geol. Sur.

seventy miles long, of much less breadth and at a distance of ten to thirty miles from the ocean. The average elevation of the region is very low, hardly exceeding ten feet above high water mark. It is freely intersected by numerous creeks, rivers and arms of the sea, in the neighborhood of which numerous marshes and swamps occur. The phosphate deposits occur most generally in what are probably old water ways, as well as in the existing water-ways. The beds themselves lie nearly horizontal and do not follow the contour of the surface. They occur at all depths from a few inches down to twenty feet or more. Two classes of deposits are recognized, namely those on the land and those in the rivers. The rock itself is usually nodular, varying in size from that of a pea up to boulders of a ton in weight, the average weight, however, being only a few pounds. The texture is porous and granular and there are many cavities and perforations in the masses. The surface is usually dull and rough. The color varies from black to dark brown. The specific gravity will average about 2.4 and the hardness 3.5 to 4.0 of the Mohs Scale.

The nodules lie in a stratum the thickness of which is from 2 to 56 inches, averaging eight or nine inches. The matrix consists of clay and sand.

The origin of these nodules must be sought in the Eocene beds underlying them. These beds consist of carbonate of lime, more or less pure, are locally called marls, and contain from 6 to 9 per cent of phosphate of lime. The various layers of the upper member of the eocene differ in their phosphatic content. In one well, the log of which was kept and the various strata analyzed, a bed of phosphate pebbles containing about 60% of phosphate of lime, was found 312 feet below the surface. The ordinary structure of the nodules and fossils imbedded therein appears to be identical with that of the underlying limestone. The underground waters contain a considerable amount of bi-carbonates and chlorides, with important quantities of free carbon dioxid in solution. The superficial waters in swamp localities carry in solution notable amounts of organic acids, derived from decomposition of the somewhat luxuriant vegetation. It has been suggested by Chazal¹ that the upper portions of the soft limestones were de-

¹ The Century in Phos. and Fert. P. E. Chazal, Charleston, 1904

tached from the original beds by various natural agencies, such as the tide, etc. and their porous nature allowed of more or less complete phosphatization by the estuarine and superficial soil waters. Hardening by this phosphatization would appear to have allowed of transportation by currents and tides, and redisposition in depressions of the bay and estuary floors. After such deposition it is possible that further phosphatization took place. Chazal also suggests that, while it is true that the beds often contain large numbers of fossils, such as bones and teeth, intermingled, but not incorporated in the nodules, the source of the phosphoric acid is by no means to be sought in such animal remains, but that the phosphatizing action has preserved such remains, and that their presence now is to be ascribed entirely to this action. It is also worthy of note that in places the upper layer of marl has been apparently decidedly phosphatized, and as a matter of fact this process appears to be still going on, a rather noteworthy instance being the recovery by a phosphate dredge of an iron hook about 5 inches long, in a fine state of preservation, around the shank of which was a continuous ring of phosphate rock. This hook apparently having fallen overboard from some vessel, the phosphatic mass has collected around it. This instance is particularly noteworthy as indicating the rapid deposition of such material, since the hook must have been dropped since the settlement of the country. It is, in a measure, analogous to action of the same sort, which has been observed in copper and iron mines.

The South Carolina rock is of somewhat low grade, running from 55 to 65% of phosphate of lime, with the iron and alumina and carbon dioxide rather high. It is admirably adapted to the manufacture of acid phosphate. For many years however, the production has been decreasing, and apparently only local consumption is now supplied. The section is of interest as being the first considerable one mined for phosphate rock in the United States, and as furnishing a basis for that industry. Following is an often quoted typical analysis of this rock:

| | |
|--|-------------|
| P ₂ O ₅ | 26.0 to 29. |
| Equivalent to Bone Phosphate of Lime | 57.0 to 63. |
| CaO ₂ | 2.5 to 5. |

| | |
|--------------------------------------|-------------|
| Equivalent to Carbonate of Lime..... | 5.0 to 11. |
| SO ₃ | .5 to 2. |
| CaO..... | 35.0 to 42. |
| MgO..... | Traces 2. |
| Al ₂ O ₃ | " 2. |
| Fe ₂ O ₃ | 1.0 to 4. |
| F..... | 1.0 to 2. |
| SiO ₂ | 4.0 to 12. |
| Organic matter..... | 2.0 to 6. |
| Moisture..... | 0.5 to 4. |

The Florida phosphate deposits are of the nodular type, in soft matrix, divided into hard rock and pebble, the latter being differentiated into "land" and "river" pebble. In addition to this there is a so-called soft phosphate which is unimportant industrially.

Topographically Florida consists of a low elevated basin, containing numerous lakes, sloping down to sea level on each side. The surface formations are sands and clays and the product of decomposed impure limestone. The elevation rarely reaches 200 feet in any place. The Peninsula is formed chiefly of limestones. These limestones are easily dissolved, being soft and porous, which fact is important in connection with the formation of the phosphate.

The "Hard rock district," so called, lies along the western Coast, in a strip 150 miles along, about twelve miles broad and distant from the Gulf from 120 to 140 miles, and practically all the mines are in the southern portion of this belt. The typical hard rock is a hard, massive, close-textured material, varying in color from light grey to blue black and in texture and structure closely resembles the calcareous sinter from hot springs. The rock occurs in pockets and in depressions, often of great size, and is produced by a solution of the underlying limestones of the slightly rolling surface of the phosphate belt. These limestones are of Tertiary age, Eocene, Miocene and Pleiocene all being represented. They are all three soft, porous, massive bedded, and rather easily dissolved. This is particularly true of the eocene which is, moreover, of great thickness. It is pervious to water and in regions where it comes to the surface there are no small

brooks and few large streams, the rain sinking into it as into dry sand. This water sinks until it meets an impervious layer or the sediment it carries clogs the pores of the stone beneath. It then flows in the direction of least resistance, forming underground brooks or tolerable streams, whose course may be marked by a long line of natural wells, and this condition of drainage according to Dall¹ has probably existed ever since the first elevation of the region. This makes very favorable conditions for the solution of carbonates and phosphates. The water in such streams is probably under considerable pressure, containing therefore a large amount of carbon dioxid, and on emerging to the open spaces of the sinks the release of pressure, or evaporation apparently results in the precipitation of the less soluble constituent, the phosphate. Continued erosion along the line of these undergrounds streams has resulted in the removal of the bridges of lime between the underground sinks. The ultimate result of such action would be the formation of open air streams, with the probable capacity to transport phosphate nodules already formed, and the concentration of them into larger beds in favorable localities. It is to be further remembered that this action is not confined to the trunk channels of the subterranean streams. The formation of phosphate probably takes place to even a greater extent in small channels and seaps, and in concentrating the nodules into considerable beds it appears likely that the subsidence and elevation undergone by the peninsular since Eocene times, which were at least aided by consequent exposure of the phosphate to waves and currents, have been important.

The result of this action has been the formation of the pockets of phosphate scattered over the Eocene and Miocene areas, generally of smaller size in the latter. These pockets are of various areas and depths, sometimes covering many acres and extending as deep as exploitation has as yet gone. Prospecting for these deposits is with post hole diggers, and dry and wet drill holes. For the former, a special type of posthole digger takes out a core of about three inches in diameter and is very efficient where there is no water. The drills, used where water occurs, are two-inch jet drills, worked mostly by hand. A

¹ W. H. Dall, Bul. 84, U. S. Geol. Sur.

small derrick is used to hold the casing, which is driven ahead of the work, and the drillings are caught by the jet out of this pipe. In mining the overburden is usually removed by hydraulic nozzles and scraper or steam shovel, the former method being the most economical. The mining of the rock itself is by hand, cars being used, to remove the rock with an incline and cable into the pits. This is the only method by which a perfect blend of the whole mine can be passed through the washer daily, and is particularly suited for avoiding the handling of dead material, such as "sand horses" and lime. It must be remembered that the nodules vary in size, and lie in a matrix largely of sand, and less often of clay. The whole country possess a fairly fixed water table and when this water level is reached this method of mining can no longer be used, and the dipper dredge is usually resorted to. The dredge barges have steel hulls about 34 feet wide and 60 to 70 feet long. The objection to the dredge is that the work is localized and an average of the whole mine can not be handled daily. Where the lumps of phosphate are small the hydraulic method has been successfully used for mining.

All this rock must be washed and dried before shipping. This is effected by passing the whole mass through a double log washer of the usual type, except where excessive clay or a large percentage of matrix is to be handled, in which case the practice is to use either another single log washer or a second double log. The rock, after leaving the washer, is conveyed to a picking table whence it goes to the driers. Formerly a kiln built of cord-wood was most used, but at present some form of mechanical drier is in favor, its use being promoted by the scarcity of fuel and labor. Owing to the occasional large size of the nodules the rock is usually broken before going into the washer, so that when it comes from the drier it is in a shape which is easily handled by hand or dipper. The following analysis is fairly typical of the Florida hard rock¹.

| | |
|--|------|
| Si ₂ O ₅ | 3.44 |
| TiO ₂ | .13 |
| Al ₂ O ₃ | 1.49 |
| Fe ₂ O ₃ | 1.43 |

¹ Clark Bul. 491. U. S. Geol. Sur.

| | |
|-------------------------------------|--------|
| CaO..... | 48.81 |
| MgO..... | .23 |
| K ₂ O..... | Trace |
| Na ₂ O | Trace |
| P ₂ O ₅ | *35.93 |
| CO ₂ | 2.71 |
| SO ₃ | .10 |
| F..... | 2.55 |
| H ₂ O at 105°C..... | .90 |
| Loss on Ignition..... | 1.98 |
| | 99.70 |

On account of its high grade and great purity the Florida hard rock has been one of the most used of all American phosphate materials, and the production, beginning about 1889, is still at a high point of tonnage. Hardly any hard rock is used in the United States, the largest part of it being exported.

The work on the Florida pebble deposits began in the year 1888 on the gravel beds of Peace River on the southwestern coast. This is the so called "river" pebble, the work on the land pebble beginning in 1889. This also lies along the west coast of Florida, but south of the hard rock district, in the Counties of Polk, Hillsboro, De Soto and Manatee. The land pebble occurs as beds of nodules, varying in size from that of a head of a pin to that of a walnut, the larger usually arenaceous. The pebbles are usually light creamy white in color, varying to brown or even black. The shape is rounded or flat ended, such as would result from attrition in water. The texture is porous, the surface of the pebbles, though usually regular, is occasionally pitted. Moreover, their somewhat pearly luster and polish appears to be due to superficial hardening. The pebbles very often show inclusions of quartz sand in grains and stringers. With the pebbles are many fossils, usually phosphatized.

These deposits lie in a clayey or sandy matrix below an overburden of sand, varying in thickness from a few inches up to many feet. The overburden is easy of removal. The underlying rock

*Equivalent to Calcium phosphate 78.47

is usually limestone, varying in character from a hard marl to a soft clay like material.

The river pebble occurs only in the streams of the southwest, including the Hillsboro river, and a few streams on the east side of the peninsula. Only on Peace river has mining been extensively carried on. The deposits there, however, are not now mined. The river pebble presents interesting points of difference from the land pebble. In size it runs usually much smaller, the individual pebble having water worn or polished surface, which are harder than the land pebble, and much darker in color, and likewise show none of the porosity of the land pebble. These changes are probably due to transportation by water, the darker color being due to organic matter derived from swamps. This pebble is of much lower grade, running only 61 to 63% of phosphate of lime.

Both land and river pebble are probably derived from a marl, or from an earthy friable limestone, being formed in small erosion channels and joint planes, left distributed thro a mass of sand or partially altered limestone, and concentrated by stream action, or where depression has taken place by tidal action. The Arcadia marl appears to underlie all the pebble phosphates. Analysis made by me shows that this marl contains something over 10% of phosphate usually, with low lime carbonate. A deposit of land pebble will often cover several hundred acres. The deposits vary in thickness from a few inches up to 18 or 20 feet, the pebbles usually representing from 10 to 15% of the whole mass. Deposits of land pebble containing millions of tons are not infrequent.

The overburden of the land pebble may be removed by steam shovels, but is profitably handled with the rock when possible, the rock itself being mined by hydraulic methods. The mining of the Florida land pebble is one of the prettiest operations in phosphate mining. The hydraulic nozzle washes the face of the deposits to a central depression or sump, at the same time partially disintegrating the matrix. The machinery except the hydraulic nozzle and centrifugal pumps, is placed upon a barge, which has previously been launched upon a pit dug to the level of the prevailing water table. The pit for mining is adjacent to the

barge and in it are placed the hydraulic nozzle and one to two centrifugal pumps. These pumps pick up the material washed to the sump, cleaning it as it passes through the pumps, and raises it to the upper deck of the barge, on which is the washing machinery, consisting simply of logs and rinsing screens. From the washer-barge the rock is conveyed either by rail or a carrying barge to the plant, where it is subjected to a further washing, and to drying by a mechanical drier. When a mining pit is worked out, the dam between it and the barge pit is broken down, the mining pit fills with water; the mining pit then becomes the barge pit, and a new mining pit is begun. The mining operations may thus make a canal from the plant to the outer limits of the field, which can be and often is utilized for the carriage of the rock to the plant.

The land pebble is a medium grade material, varying usually from 68 to 72% of phosphate of lime, but within recent years deposits west of Lake County have been opened which are of higher grade, containing from 72 to 76% of phosphate of lime. The following is given by Eldridge¹ as a typical analysis of the washed pebble.

| | |
|--------------------------------------|--------|
| Insoluble matter..... | 6.69% |
| Moisture..... | .79 |
| Loss on ignition..... | 3.47 |
| CO ₂ | 3.93 |
| F..... | 1.86 |
| Al ₂ O ₃ | 2.14 |
| Fe ₂ O ₃ | .61 |
| CaO ₂ | 46.03 |
| MgO..... | .33 |
| P ₂ O ₅ | 31.50* |

Much the larger part of the land pebble is used in the United States but a considerable proportion of it, particularly that of the higher grade, is shipped abroad. The production of land pebble has increased very greatly within the past few years and now

¹ Trans. Amr. Insti. Ming. & Eng. Chem. Vol. 21

* Equivalent to Calcium Phosphate, 68.76.

furnishes the largest part of the phosphate of lime produced in the United States.

The so-called "white rock" of Tennessee occurs in the valley of the Tennessee river in the western part of the State, in the Counties of Perry, Decatur, Benton, etc. In appearance it differs little if at all from the Florida "hard rock," and the grade is about the same or a little bit lower. The deposits were formed apparently in open caverns or depressions in the underlying limestone, which is soft and easily eroded. The exact period at which the deposits themselves were formed has not been determined, and the source of the phosphatic matter is a little obscure, but the best hypothesis regarding it is that it is derived in greatest part from the overlying Devonian bedded phosphates, which have been removed where this white rock occurs. The topography of the country is hilly, with small streams cutting comparatively deep valleys, and on the hillsides in the lower levels of the valleys this rock is usually found. It will be noted therefore, that it owes its presence largely to the same forces which formed the Florida hard rock. The present extent of the deposits of this material is unknown, but as efforts have been made since about the year 1895 to develop them, apparently without success, there is evidently some serious commercial or geologic difficulty to be overcome.

The only nodules occurring in a hard matrix are those of the upper Devonian of Tennessee. They are best treated in connection with the next class.

The stratified phosphates constitute, because of recent discoveries in the United States, and because of the importance of the North African deposits, by far the most important class of phosphate rock now known. Moreover these deposits far exceed in amount any of the other classes. I have made a separate class of the phosphatic-limestone beds, because of the large number and almost invariable association of phosphates and phosphatic limestone, as well as because of the fact that this class is directly the cause of some of our most important industrial phosphates.

Taking up first the class of unleached deposits, only such limestones are considered as are capable of direct industrial application for the sake of their phosphatic content. The only deposits

of this character which are of importance in the United States are those of the Ordovician of Tennessee and Kentucky.

Such deposits exist in central Tennessee and in central Kentucky. In Kentucky, in which the deposits are of minor importance, the town of Midway in Fayette County, may be considered as a center. In Tennessee these limestones exist in varying degrees of purity all over the so-called Central Basin, of which Nashville is near the geographic center and which has an extent of ten or twelve thousand square miles. The center of their formation may be taken as at Mt. Pleasant, some fifty miles south west of Nashville. The topography of this country is rolling, with ranges and isolated hills three or four hundred feet high, outliers from the rim of the basin. The phosphatic limestones themselves have a thickness of 200 to 400 feet. Fairly pure phosphatic limestones occur at intervals throughout this range, but the most important being the so-called Bigby limestone, lying near the bottom of the series and with a thickness of thirty to one hundred feet, and from the Bigby practically all the "brown" phosphate rock which has been shipped from Tennessee has come.

The phosphatic material in the unaltered limestone beds is usually granular, rather dark blue in color, forming laminae of varying thickness, with the content of phosphate of lime up to as high as 50%. At times this highly phosphatic portion of the limestone may form practically all of the bed. No use is made at this time of this material, but in view of the increasing tendency to apply raw phosphates to the soil, this limestone may very soon develop into an important industrial product.

Leaching from these limestone beds has given rise to the very important so-called brown phosphate of Tennessee and Kentucky. The Tennessee deposits discovered in 1896 were immediately worked and development has been going on rapidly since that time. The typical deposit of this material resembles a loosely built wall of dry masonry, the spaces between the places of the phosphates being occupied usually by a clay or sandy loam, containing a considerable proportion of the phosphate in the form of fine sand. The conditions necessary for the formation of this material from the parent limestone are an exposure of a

considerable area of the limestone, with moderate porosity in the underlying bed, to afford free passage through the phosphate stratum of the circulating waters of the soil. Weathering has taken place along joint planes or other planes of weakness, and usually a core of the limestone is left within the quadrangle of the joint planes. The formation of this phosphate is one of the best illustrations known of the general principles of phosphate deposition.

The rock itself is a material grey to dark brown in color, very porous, usually in plates, varying in size with the size of the parent layer, and occasionally running as high as several hundred pounds. The texture is granular, the actual specific gravity is about 2.8, the apparent specific gravity being much less on account of the porosity of the material. The hardness is very low, and the rock may at times be broken with the fingers.

The prospecting for this material is done by means of an earth auger, and pitting to confirm the indications of the auger. Great care must be exercised in prospecting, due to the fact that different layers of the Bigby furnish rock of different grades and the prospector is apt to confuse them. The rock stratum varies in thickness from a few inches up to several feet. The overburden may go as high as thirty feet, and consists chiefly of clays. The usual rule in the district is that if overburden does not exceed ten feet for each foot of rock, it may be mined advantageously, but of course this would not apply beyond certain limits. The majority of the stripping is done by wheeled scrapers, but machines are now being more generally used. Steam shovels are being applied to advantage by some miners, while one important installation used a long boom revolving shovel with drag line scraper. One concern is removing the overburden by hydraulic means, to advantage. The mining is altogether by hand, machine being used only for conveying the rock to the plant.

The preparation of the rock consists of washing with water, after separating the lump from the fine material. The fine material is washed in several waters, or otherwise treated so as to remove the clay and sand. It is noteworthy that all the fine material, up to about the year 1908, was lost, going usually into the mud ponds, but occasionally being covered up in such a way

that it would cost more than it is worth to recover it. The latter material is of course permanently gone. For ten or twelve years the mining of brown rock in the Mt. Pleasant district was one of the most wasteful processes imaginable. The fine material rejected at that time is now being worked over. One concern, for instance, has extracted in the neighborhood of 100,000 tons of the material from a single waste-pond. Following is a typical analysis of a very high-grade Tennessee Brown rock.

| Constituents | Bigby Rock from Mt. Pleasant, J. H. Pratt Analyst, | Average of about 1000 samples of all sorts over sev- enty five percent Bone Phosphate |
|--|--|---|
| Moisture..... | 37.73 | 36.25 |
| Phosphoric acid..... | 82.63 | 79.17 |
| Equivalent to tricalcium phosphate (bone phosphate)... | 1.72 | } 4.28 |
| Alumina..... | 1.19 | |
| Equivalent to aluminum silicate..... | 1.89 | |
| Carbon dioxide..... | 1.05 | |
| Equivalent to Calcium Carbonate..... | 2.39 | |
| Sulphuric Acid..... | 0.84 | |
| Equivalent to Calcium Sulphate..... | 1.42 | |
| Silica (sand)..... | .20 | |
| Magnesia..... | .19 | |
| Equivalent to Magnesium Silicate..... | .33 | |
| Organic matter and combined water..... | 2.33 | |
| Fluorin..... | 2.07 | |
| Equivalent to calcium fluorid | 4.23 | |
| Calcium oxid combined with organic acids..... | 2.69 | |
| Manganese Dioxid..... | .10 | |

| | |
|---|-----|
| Titanic acid..... | .12 |
| Alkalies (oxids potassium and sodium)..... | .30 |

Apparently the larger part of this typical phosphate has been mined, and this fact up to some three years ago gave the operators serious concern, until a method was worked out for washing the comminuted phosphate matter from the loam with which it is mixed. Space does not allow of a complete description of this important improvement. Suffice it to say that well known principles of ore washing have been applied, some of them in a novel way. It is to be noted that by this means a recovery in phosphate of from 25% to 50% of the whole mass is attained, the lost material being finely divided clays and sands. It is to be noted that from ten to twenty per cent of the whole exists as a very finely divided form of phosphate, from $1/60$ to $1/200$ of an inch, and that the endeavor at this time is chiefly to save this finely divided material, with considerable prospects of ultimate success. The recovered material ranges in analysis from 70 to 80% of phosphate of lime, but the impurities, oxides of iron and alumina are rather high, as compared with the Florida product, being from three to six per cent. There is comparatively little demand on the market for the lower grades of this material, usually a seventy five per cent product being called for. The very large amount of low grade phosphates, the impurities of which are clay and sand, which exists within the area mentioned will doubtless be utilized.

The higher grades of this material have been shipped abroad, but at present this demand takes only ten to twenty per cent of the whole production, much the larger part of it being utilized in the United States, and when properly handled it is a good material for the manufacture of acid phosphate, being especially easy to grind.

A noteworthy modification of these deposits belongs to the class of nodules in soft matrix. These deposits appear to resemble in their origin the hard rock deposits of Florida, likewise resembling this rock in appearance, except for their dirty brown color. They were deposited from water in cavities as well as in pockets along the course of joint planes. Their total is small and they are of little value industrially.

Turning now to the pure but unleached stratified beds, these are distinguished by the fact that they form an integral part of the stratigraphy of the country, that they were therefore deposited of the quality and in the form in which we now find them, and, what is quite important, that they do not require washing or other preparation between mine and factory.

One of the most notable of these is the so-called "blue rock" of Tennessee. This belongs in the lower part of the Devonian, which is very persistent in the Mississippi basin, although usually of no considerable thickness. The bulk of this formation consists of a sharply defined bituminous shale, known locally as "The Black shale." This is rarely more than twenty five or thirty feet in thickness, and the phosphate itself, lying below, will range up as high as (an exceptional thickness) three feet. Typically the phosphate is grey to blue black in color; texture fine grained up to grains large enough to be seen by the naked eye; hardness about the same as that of the South Carolina rock, with a specific gravity of about 2.8. The rock therefore, very greatly resembles oolitic limestone in appearance. It was discovered in 1893, working began in 1894 and has continued ever since. Comparatively little of the blue rock, however, was mined during the years from 1896 to 1901, owing to the large supply of the brown rock discovered at that time, which was more cheaply mined. The Devonian phosphate bed rests usually upon limestones of Silurian or Ordovician age.

The calcium phosphate of the material runs from 60 to 70%, the latter being somewhat exceptional. The following is an incomplete analysis of a high-grade specimen.

| | |
|---|-------|
| Moisture | 1.40 |
| Insoluble matter | 3.16 |
| Fe ₂ O ₃ | .99 |
| Al ₂ O ₃ | .86 |
| FeS ₂ | 3.62 |
| CaCO ₃ | 4.20 |
| CaSO ₄ | 5.65 |
| P ₂ O ₅ | 33.43 |
| Equivalent to Calcium Phosphate | 72.92 |

The rock is characterized by the presence of pyrites, resembling in this particular the Carolina rock. Calcium sulphate for the most part appears to be present in greater or less amounts. Since the rock is high in organic matter it is to be presumed that the presence of the phosphate is due to the same conditions which produced the organic matter.

The topography of the country in which it occurs is hilly, the rock outcropping usually a few feet above the beds of the streams, and above it lie, ordinarily, 100 or more feet of shales, siliceous limestones and cherts. All the strata in Tennessee lie approximately horizontal, so that the mining of this is more nearly like that of a horizontal coal seam than like any other common form of mining work. Under ordinary conditions it pays to work a seam not more than 12 inches thick, provided it is of the right quality. The material is excellent for the manufacture of acid phosphate, but apt to be somewhat erratic in its occurrence and composition.

The derivation of this material is most interesting. According to Hays and Ulrich (and in the writer's opinion these gentlemen are unquestionably correct) a large part of the Ordovician land surfaces were elevated above sea-level after being laid down. The same kind of open-air and subterranean disintegration took place, that we have found has produced the present brown rock, so that in effect brown rock beds were produced. Subsidence then took place, but the sea was comparatively shallow and received drainage from still elevated land areas. The Devonian sea, as is well known, was rich in organic life, both animal and vegetable. Gentle currents must have prevailed, probably in sheltered bays or estuaries, sufficient to remove the clays and sands in large part from the disintegrated phosphate, but not sufficient to carry off the somewhat larger phosphate grain. The seas themselves were likewise rich in phosphates. Therefore where the Ordovician phosphatic limestones had not been covered by subsequent formations, or where such formation had been taken off by erosion leaving the phosphatic limestones as the surface rock beds, blue rock was formed. Where on the contrary surface rocks were Upper Ordovician or Silurian, the phosphate beds are impure and apparently the phosphate was derived only

from the phosphatic material of the Devonian Seas, mixed with clays or sands. The blue rock, therefore, is found of merchantable grade only where the underlying rock is the Ordovician phosphatic limestone. Occasionally the mass of blue phosphate, likewise, will be found surrounding a low core of unaltered Ordovician limestone in the same way as the brown rock phosphate now surrounds a core of the same limestone. It is therefore useless to expect merchantable blue rock underlaid by any except the latter formation.

It is impossible to separate in the statistics the shipments of blue rock and brown rock, but by far the greatest part of phosphate shipped from Tennessee is of the Brown variety. Finally, the underlying limestone of the blue rock beds is not necessarily of the Bigby series, but may be of the Leipers, which is the upper phosphatic horizon of the Ordovician.

Lying at the upper limit of the Devonian is a bed of soft shale rich in organic matter, and probably a deep water formation, representing therefore the last phase in the formation of the Devonian Seas, which contains concretionary nodules of phosphate of lime. These differ from the South Carolinian nodules in being of comparatively smooth surfaces, with fairly regular outlines. The typical shape is oval and the concretionary structure, on fracture, appears marked. These nodules are of varying grade and often rich enough to be of value. They are so rich in organic matter that spots of oil often appear on a fresh fracture, being quickly absorbed again, however, by the rock. This layer exceptionally is as high as two feet in thickness and thirty per cent of the mass may be phosphatic nodules. It is reported that the matrix quickly slakes on exposure to the air, permitting the screening out and separation of the nodules. At present none of the material is on the market.

The so-called hard rock of Maury County has been exhausted, so is purely of scientific interest at this time. It was a local concentration of lime phosphate in the Bigby beds of phosphatic limestone, the scientific interest proceeding from the fact that indicates the ultimate extent to which phosphatization of these limestone beds has proceeded. It appears to closely resemble the blue rock beds in structure.

The bedded phosphates of Arkansas occur in the western edge of Independence County, and in the adjoining territory, with an East and West extent of about eighty miles. Only, however, at isolated places do deposits sufficiently rich or large to mine occur. They are associated with the Cason shale, which in this section is the upper member of the Ordovician. At only one place are they now being mined, and here the thickness varies from four and one-half to six feet, with a low grade bed of four feet below the rich bed. The deposits being worked are a compact homogeneous light grey rock, with a specific gravity of about 3. An Oolitic texture, is frequent in some places, the oolites being one-fourth of an inch in diameter, giving the rock a distinctively conglomeratic appearance.¹ The material is of rather low grade, running from 60 to 65% phosphate of lime. As suggested the production is small and is used only locally.

The largest phosphate deposits in the world have within the last eight years been developed in the Rocky Mountain region on both sides of the Boundary between Wyoming and Idaho. They are said to have been first recognized by two analyses made in 1897. The first development of consequence was in 1904 and 1905, and they have been thoroughly investigated by the United States Geologic Survey.

Just as the horizon furnishing the blue rock of Tennessee, which is phosphatic in practically its whole extent, extends from Pennsylvania to Oklahoma, so in the western phosphate belt, phosphate of some grade is found from the eastern part of Wyoming to the eastern part of California, and as only in certain parts of Tennessee, is blue rock of value found, so in certain parts only of the western field does high grade phosphate occur. Deposits are known in north eastern Utah, southwestern and western Wyoming, north eastern Idaho and western Montana. The developed workable beds occupy an area of probably two hundred miles long by forty to sixty miles wide.

The country is an elevated plateau, occupied by ranges of mountains from one thousand to four thousand feet higher than the general surface. The mountain-making forces have of course been active, and the strata stand at all angles from horizontal to

¹ A. H. Purdue, Bul. 315 U. S. Geol. Sur.

perpendicular. The phosphate deposits, of course, do not occur over all the area in which they may be found, but do occur except where they have been removed by erosion, or by faulting or other disturbances. Geologically the deposits occur in the Park City, the uppermost member of the Pennsylvanian, which in turn is the upper member of the Carboniferous rocks of the West. This whole formation, according to Richards and Mansfield¹ is divisible into three units, as follows; at the bottom, a light bluish massive limestone; next the phosphate series, consisting of phosphate rock, phosphatic shale, and minor limestone bands, and uppermost a cherty limestone. Richards and Mansfield gave many sections of the phosphate bed. The whole series varies from 90 to 200 feet in thickness. Thus in a complete section in Georgetown Cañon Idaho, this formation was 140 feet thick and there were only five feet of it which did not contain an appreciable amount of phosphate, ranging from $7\frac{1}{2}$ to 82% of phosphate of Lime. Of this thickness there were four separate beds, aggregating $18\frac{3}{4}$ feet, none of which ran below 70% Bone Phosphate. A section in Bannock County Idaho showed a total exposed surface of the phosphate series (the rest being concealed by drift of fifty feet, of which 7 feet showed a phosphatic content of 72%. A few miles further north the writer, following a crosscut 28 feet long, found six feet of phosphate rock running over seventy per cent, eight feet from sixty five to seventy per cent, and four feet sixty to seventy per cent, in five separate layers. The Park City formation then must be looked upon as phosphatic shale and limestone beds, alternating with beds of phosphate, the average total thickness of which has never been determined, but is probably not less than ten feet of merchantable rock in any one place.

This rock resembles the blue rock of Tennessee more than any other American formation. It is oolitic in texture, the oolites being bound together by a mass of more finely divided phosphate, with a small amount of clay or sand. The specific gravity is from 2.8 to 3. The material contains a considerable amount of organic matter and a small amount of carbon dioxid. The oxids of iron and alumina, very rarely, so far as the writer's experience

¹ Bul. 438-70 U. S. Geol. Sur.

goes with several hundred maples, runs over 2%. The following analysis given by Gale and Richards¹ appears to me to be typical

| | |
|---------------------------------------|----------------|
| Insoluble matter..... | 2.62 |
| SiO ₂ | .46 |
| Al ₂ O ₃ | .97 |
| Fe ₂ O ₃ | .40 |
| MgO ₃ | .35 |
| CaO..... | 48.81 |
| Na ₂ O..... | .97 |
| K ₂ O..... | .34 |
| Moisture..... | 1.02 |
| Combined..... | 1.34 |
| TiO ₂ | None |
| CO ₂ | 2.42 |
| SO ₃ | 2.16 |
| F..... | .4 |
| Cl | Trace |
| Organic matter..... | Not determined |
| P ₂ O ₅ | 33.61 |
| Equivalent to Phosphate of Lime | 73.42 |

Some of the rock runs considerably higher in phosphate of lime. The origin of these deposits has not as yet been satisfactorily worked out. Richards and Mansfield suggest that indications point to a direct physical and chemical origin for them, rather than to an origin in which organisms of any character play a prominent part. This presupposes a sea of a high content of phosphoric acid and conditions which precipitated this phosphoric acid as phosphate of lime. In this connection the high content of organic matter is apparently of significance.

The market for this rock at present is almost altogether on the Pacific Coast, and the consumption of fertilizers there appears to have been greatly stimulated by its discovery. Unquestionably, as the soils of the Mississippi and Missouri basins, and the Inter-Mountain district wear out, the demand for it will become great. The outcrops of the rock occur on the sides of the mountains and foot-hills. The mining is practically all underground

¹ Bul. 458 U. S. Geol. Sur.

and is extremely cheap. Work so far done indicates that it can be put on board the cars for much less than \$1.00 per ton.

Practically all this rock occurs on lands owned by the Government of the United States, and in 1908 President Roosevelt withdrew these lands from further entry under the United States mineral laws, this action having since been confirmed by Congress. Prior to that time, however, several thousand acres had been entered by various persons, and such entries constitute that portion of the field which is now being worked. The rock is a material which leaves little to be desired for the manufacture of acid phosphate, and there is little prospect of the early exhaustion of the deposits, since estimations by the United States Government indicate a thousand million tons or over which is close enough to the surface for economical mining, at this time.

The class of impure but unleached stratified beds, comprise the impure blue rock of Tennessee and the Devonian of Arkansas, which is too poor for working, and the shales of the Rocky Mountain region. They may be regarded as reserves of phosphate materials to be worked when the purer phosphate are exhausted.

The phosphates apparently due to Terrestrial animal life, comprises the soluble Guanos of various derivation, such as those from birds or bats, the phosphates being due to the decomposition of the guano of birds, on Rocky Islands in a region with rainfall, with subsequent leaching of the phosphoric acid into the underlying rock. Where this rock is limestone, phosphate of lime occurs. Where it is a trachyte or other igneous rock, phosphate of alumina is the prevailing compound. The island deposits of the Pacific Ocean, such as Makatea, Nauru, etc., appear to be due to the former case. The deposits of Connetable Island are examples of the latter. Such deposits, while often of large extent, are usually not comparable in quantity to the large deposits of the Rocky Mountain region, or Florida or Tennessee.

Besides the deposits which have been described there exists in practically all the states of the Atlantic Seaboard and the Gulf of Mexico, isolated deposits of nodules in small amounts in the Cretaceous rocks. Some of these nodules are of high grade, but because of their variable quality and the very small amounts in which they occur, encouragement to prospectors has not been

sufficient to justify extended work. It is of course possible that deposits of this character of sufficient amount and grade may ultimately be discovered.

Finally, it is of interest to note that since the beginning of phosphate mining in this country on a commercial scale in 1867, there have been mined according to the U. S. Geological Survey 39,640,810 tons of rock, valued at \$162,329,000. Of this total South Carolina mining since 1867 has produced 11,200,074 tons; Florida mining since 1888 has produced 20,371,290 tons; and Tennessee mining since 1894 has produced 6,483,983 tons. The present relative importance of the different sections is given by the following table of production in 1911.

| | | |
|-------------------------------|------------------------|--------------------------|
| Florida hard rock..... | 443,511 | Tons |
| Average price per ton..... | \$6.23 | |
| Florida land pebble..... | 1,992,737 ¹ | |
| Average price per ton..... | \$3.37 | |
| | | |
| | Quantity (long ton) | Average price per ton |
| Florida hard rock..... | 443,511 | \$6.23 |
| Florida land pebble..... | 1,992,737 ¹ | 3.37 |
| | | |
| Total | 2,436,284 | 3.89 |
| South Carolina land rock..... | 169,156 | 3.98 |
| | | |
| Tennessee Brown rock..... | 365,068 ² | 3.97 |
| Tennessee Blue rock..... | 72,302 ³ | 3.65 |
| | | |
| Total..... | 437,370 | 3.92 |
| Western States..... | 10,505 ⁴ | 3.80 |
| | | |
| Grand Total..... | 3,053,279 | \$3.90 |

It is to be noted from the above that both Arkansas and Kentucky have produced very small amounts of rock.

¹ Includes small quantity of river rock.

² Includes a small quantity from Kentucky.

³ Includes Arkansas

⁴ Includes Idaho, Utah and Wyoming.

(*Abstract*)

A STUDY OF THE VARIATIONS IN CHEMICAL COM-
POSITION OF THE TIMOTHY AND WHEAT
PLANTS DURING GROWTH AND
RIPENING

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PLAN OF THIS WORK

Definite areas from a timothy field and a wheat field were harvested at certain definite stages of growth, the entire plant being removed at each cutting. With the timothy, samples representing six stages were collected ranging from time before the heads appeared to the time the seed was fully ripe. One extra collection was made of the bulbs about the time growth started in March of the following year, making seven stages in all. Samples of wheat were collected in four stages of growth starting from the time the head is formed until the time of ripe wheat.

The timothy plant was separated into four parts for analysis as follows: heads, stalks with leaves, stubble, and bulbs; the wheat was divided into three parts as follows: heads, stalks with leaves, roots with the stubble. Upon each sample thus obtained the following constituents were determined both for the timothy and wheat samples: moisture, protein, fat, crude fibre, ash, nitrogen free extract. In addition potassium oxide and phosphorus pentoxide were determined in the ash of each of the samples of the timothy parts. The results are given in percentages upon the water free basis, and in pounds of each of these constituents per acre of the plant.

SUMMARY

1. The timothy plant takes up its plant food, nitrogen and ash constituents, at the most rapid rate in the young stages.

It continues at a decreasing rate to absorb plant food during growth and in about the same rate as this growth proceeds. The per cent of moisture in the green plant is also the highest in the young stages.

2. The heads of timothy increase in dry matter throughout the growth and ripening period. This increase includes all the plant constituents except potassium oxide which has reached its maximum amount before the heads were collected for analysis in Series 3. Nitrogen free extract increases at the greatest rate of all constituents. As the heads approach full ripening a noticeable increase of phosphorus pentoxide occurs.

3. The stalks of the timothy increase in dry matter during growth and ripening: this dry matter added consists chiefly of crude fibre and nitrogen free extract. Nitrogen, ether soluble material, potassium oxide and phosphorus pentoxide increase during growth but decrease to some extent during ripening.

4. The bulbs increase in dry matter throughout the growth period, but the amount becomes constant before ripening of the hay. The material stored up is principally nitrogenous matter and nitrogen free extract. No starch is produced in the bulbs during the storing process. Potassium oxide is found in maximum amount in the first stage but phosphorus pentoxide tends to increase in amount as the plant matures.

5. Large amounts of available "potash" and "phosphoric acid" are required for a good yield of timothy. Timothy would hardly prove a profit yielding crop on soils other than those rich in "potash" especially where the mineral elements would have to be supplied in the form of fertilizer.

6. The wheat plant also takes up its principal plant food—nitrogenous and mineral matter—at the greatest rate in the young stages and at a decreasing rate as growth proceeds. The highest per cent of moisture in the green plant is found in the first series.

7. The heads of the wheat gain more uniformly and rapidly in their amount of dry matter than any other part. Nitrogen free extract is produced and stored at a greater rate than any other constituent, but nitrogen, ash and ether soluble matter are added in some quantity also. Fibre is practically all formed

by the time the blossom has fallen and remains constant to ripening.

8. The wheat stalks contain their maximum amount of dry matter at blossoming time after which they pass some of this material along to the ripening heads. Nitrogenous substance and nitrogen free extract appear to be the constituents which the stalks yield up to the heads.

9. The wheat roots and stubble increase in dry matter up to the milk stage after which it decreases in amount, being passed along to the plant above ground. Fibre present in the roots does not decrease in amount but nitrogenous and ether soluble material, ash, and nitrogen free extract pass out of the roots into the growing plant above ground during the ripening of the heads.

BEHAVIOR OF AMINO ACIDS IN THE SOIL

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Investigations concerning amino acids must be of unusual interest to biochemists when we consider that by far the greater part of the protein molecule is made up of amino acids. This is true not only of proteins found in the animal organisms, but of those occurring in plants just as well, since generally speaking the same amino acids, though in different proportions, are found in protein bodies of either animal or vegetable origin. The latter fact is agriculturally of great moment inasmuch as the experience gained by numerous investigations on animal protein can advantageously be applied to proteins or their decomposition products present in soils or plants. Yet until comparatively recently the chemical nature of the proteins themselves was practically unknown.

It is true that as early as 1873 the fundamental work of Hlasi-vetz¹ and Habermann revealed the important fact that the amino acids: leucine, tyrosine, aspartic and glutamic acids were contained among the hydrolytic products of casain, albumin and other proteins. It is also true that the researches of Kossel², Kutscher and their co-workers have shown that the diamino acids arginine, histidine and lysine were contained among the decomposition products of most of the protamines and proteins which they have investigated. But it is equally true that the work of these authors, important as it was, did not give us yet an idea as to how the amino acids were linked together in the protein molecule. This was accomplished by the excellent researches of E. Fischer and his school. Not only was he able, by what has become to be known as the Fischer³ ester method, to add several

¹ Ann. Liebig 169, 150.

² Zeit. physiol. Chem. 22, 176; 25, 165; 25, 551; 26, 586; 26, 588; 28, 382; 31, 165; 33, 347; 38, 39; 40, 311; 41, 407; etc.

³ Zeit. physiol. Chem. 33, 151; 33, 412; Ber. 35, 2660.

more amino acids to those already known, but—what is of vastly greater importance—the investigations¹ in question revealed the structure of the protein molecule. As a result of all the above investigations we now know that all proteins, no matter how large their molecules may be, when hydrolyzed, chiefly yield amino acids and ammonia, which latter, as was shown by Osborne, usually results from the dicarboxylic acids which are present in the protein molecule in the form of acid amid radicles; that the amino and carboxyl groups of the various amino acids are alternately coupled with one another; that proteins differ from each other either because they contain in their molecule different amino acids, or different proportions of them, or because the amino acids are linked together in a different way.

As far as decomposition of proteins in the soil is concerned, it is to be stated that the facts so far secured are not yet sufficient to give us a clear picture of the chemical processes involved. To demonstrate them experimentally would undoubtedly be of great value to both science and practice.

Elsewhere² it was outlined that decomposition of protein bodies contained in soil organic matter can be accomplished through bacterial activity, the agency of enzymes or even by purely chemical means. It was further pointed out that it would be most natural to assume that the disintegration in the soil is primarily protein hydrolysis, *i. e.*, that the proteins present in the soil are gradually broken up³ to albumoses, pepetones, acid amides and amino acids. The latter are the organic nitrogenous compounds out of which ammonia is formed in order to be oxidized further to nitrites and nitrates.

Inasmuch as it was demonstrated by the writer⁴ and others⁵ that the bulk of the acid-soluble nitrogen in the soil is made up

¹ Untersuchungen über Aminosaüren, Polypeptide und Proteine, by E. Fischer, Berlin, 1906.

² Iowa Agr. Expt. Sta., Research Bull. 1, 5; (1911).

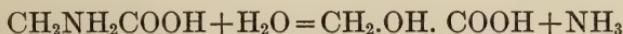
³ Ibid.

⁴ Journ. Amer. Chem. Soc. 32, 396; 33, 1226; 34, 94; Also Mich. Agr. Expt. Sta. Technical Bull. 4 (1909); Iowa Agr. Expt. Sta. Research Bull. 1 (1911) and Res. Bull. 3 (1911).

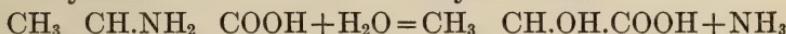
⁵ Vers. Stat. 56, 311 (1902).

of acid amides and amino acids, which are the organic substances immediately preceding the ammonia production, it is at once evident that direct experiments having as their object to throw light upon the behavior of amino acids in the soil are of considerable interest to agricultural science as well as to practical agriculture.

One of the questions arising here is: Do the amino acids in the soil split off their nitrogen by a simple hydrolytic process, or is the deamination an oxydative one. In the first case we would have, for instance, the following reactions:



Glycocolle Glycolic acid



Alanine Lactic acid

Some of these hydroxy acids and especially the fatty acids which can also be formed from the amino acids may give rise to accumulation in the soil of acidity which is detrimental to plant life. On the other hand, if the deamination is an oxydative hydrolysis leading more or less quickly to a complete destruction of the molecules, then deterioration of the soil through acids would not follow. On the contrary, the soil atmosphere would be enriched in carbon dioxide—an important plant food—just as the soil is benefitted by the formation of ammonia out of the amino acids.

It is with the production of ammonia from amino acids and acid amides that we are primarily concerned in this paper. The process of ammonification as well as of nitrification and denitrification was first systematically studied by Remy¹ who used the solutions of peptones, ammonium sulfate and nitrites for measuring the activities of bacteria producing ammonia, nitrous and nitric acid respectively. It is to this method and its modifications that we owe a very considerable part of our present knowledge concerning the processes of ammonification, nitrification and denitrification.

However, the so called solution method as used by bac-

¹ Centbl. Bakt. etc., 2 Abt. 8 (1902), pp. 657, 699, 728, 761.

teriologists has disadvantages chief among which is the fact that it creates conditions not similar to those existing in the soil. For this reason the use of the soil as cultural medium is to be considered as a further important step in that direction. The main value of the method consists in that it allows to estimate the available nitrogen inorganic nitrogenous substances, such as tankage, dried blood, cottonseed meal, ground fish, bone meal, etc., whose nitrogen is more or less readily transformed in the soil into ammonia nitrites and nitrates. It is by the application of the latter method that a good deal of work has been accomplished in this country, especially by Lipman¹ and his co-workers. However, the addition of definite amounts of organic nitrogenous materials to the soil and determination after a certain period of the ammonia, nitrites and nitrates produced requires, say, from four to twelve days, in the case of ammonia, and from three to eight weeks or more in the case of nitrites and nitrates. Furthermore, the results obtainable with this method differ, not infrequently quite considerably, if, for instance, different soils be applied as cultural medium.

A chemical method for determination of the available nitrogen, could it be devised, would require but a few days and would give more accurate results. This article is the first contribution in that direction.

Of course, for working out such a method it is necessary, first of all, to know all the organic nitrogenous compounds occurring in soils, and in the second place, to learn how much of their nitrogen is available, *i. e.*, is capable of being converted in the soil into ammonia or nitrates. The problem seems, at first sight, to be a complicated one. However, a closer consideration of the results already accomplished is of rather encouraging nature. As was outlined by the writer² in 1909 the nitrogen in (peat) soils must be made up of proteins or their decomposition products, since soil humus is chiefly the result of decaying plants all of which contain proteins. In conformity with this view it was experi-

¹ See, e. g., Report of the Soil Chemist and Bacteriologist of the New Jersey Agr. College Expt. Sta. for the years 1907, 1908, 1909, and 1910.

² Michigan Agr. Expt. Sta. Tech. Bull. 4.

mentally¹ demonstrated that practically all the acid-soluble nitrogen in Michigan peat soils consists of acid amides, diamino-acids and monoamino acids. All later investigations within our reach confirmed² those facts, as far as organic nitrogen in soils is concerned. The extraction from soils of cytosine³ xanthine,⁴ hypoxanthine⁵ all of which are cleavage products of nucleoproteids and nucleic acids, as well as of creatinine⁶ resulting from breaking up of albumin, also belongs to the same category of protein products. The above being true, it is clear that a chemical method for determination of the available nitrogen in soils will have to be one which permits of separating the protein decomposition products into the various classes of compounds already known. The Hausmann⁶-Osborne method as applied to soils by the author, perhaps in combination with the formaldehyde titration method of Sörensen,⁷ or with the nitrous acid method of Van Slyke⁸ seems to be here most promising.

In the first place the question is to be answered as to whether all amino acids, known to occur in proteins, equally readily split off their nitrogen in the soil in the form of ammonia, also how fast they do it, and finally whether the deamination is a quantitative one.

From theoretical considerations it may a priori be assumed that deamination in the soil of purely aliphatic amino acids is likely to be different from deamination of heterocyclic compounds, such as proline and oxyproline, or of amino acids containing the NH₂ group in the side chain of the benzene ring, such as tyrosine and phenylalanine.

If the deamination of the amino acids is a simple hydrolytic process, then any considerable differences in the ammonification of the various amino acids should naturally not be expected.

¹ Ibid.

² Journ. Amer. Chem. Soc. 33, 1226; 33, 564; 34, 94.

³ Jour. Biol. Chem., Vol. 8, No. 5, p. 385.

⁴ Ibid.

⁵ Journ. Amer. Chem. Soc., 33, 2035; 34, 99.

⁶ Zeit. physiol. Chem. 27, 95; 29, 136; also Journ. Amer. Chem. Soc. 25, 323.

⁷ Biochem. Zeit. 7, 45; 7, 407; also Journ. Amer. Chem. Soc. 33, 1236.

⁸ Proc. Soc. Exp. Biol. and Med. 7, 46 (1910); also Berichte d. D. Chem. Ges. 43, 3170 (1910).

If, however, simultaneously with the deamination, also a breaking up of the whole molecule takes place, then it is reasonable to expect that amino acids of similar structure, like, e. g., glycocoll and alamine on the one hand, aspartic acid and glutamic acid on the other, will ammonify with about the same intensity, and that amino acids with the resistant benzene ring, like tyrosine and phenylalanine, will ammonify more slowly, provided the physical and bacteriological factors in the soil remain the same. The above deductions were in part confirmed by the experiment. Since factors like moisture, temperature, air, etc. have great influence on decomposition of organic matter, it was thought necessary to carry out the experiments under uniform conditions which fairly closely approach those existing in the soil, in order to be justified to draw more general conclusions from the comparable results thus secured. Accordingly, we kept the soils treated with amino acids always at room temperature, the moisture of the soils was throughout the experiments uniformly about eighteen per cent, the soils were always placed in covered tumblers or in beakers covered with Petri plates, in each case allowing sufficient circulation of air for maximal activity of the microorganisms. Other conditions as well as details will be found in the experimental part.

EXPERIMENTAL

The soil which was used for the experiments reported in the following pages is one composed of samples taken from twenty-two plots of the Agricultural Experiment Station field which is located on the Wisconsin drift. While the soil employed in the experiments of the Series I, II, III and IV, was taken from the above plots in the fall of 1910, the soil used for the Series V, VI, and VII was secured in the fall of 1911.

The plots were treated with various organic materials¹ such as manure, peat, timothy, clover and grew a variety of crops, namely; corn, oats, timothy and clover. At the time when this investigation could be taken up the average soil samples of all

¹ The exact treatment of the plots, as well as their cropping is given in Iowa Agr. Expt. Sta. Research Bull. No. 3, p. 123.

the plots got for 1910 and 1911 respectively showed the following composition.

| | Moisture Per cent | Total nitro- gen. Per cent of oven-dried soil | Ammonia nitrogen. Per cent of total nitrogen | Nitric nitro- gen. Per cent of total soil nitrogen |
|-------------------------------------|----------------------|--|---|---|
| Average Soil Sample of 1910..... | 18.45 | 0.302 | 1.74 | 3.22 |
| Average Soil Sample of 1911..... | 18.68 | 0.296 | 1.63 | 2.66 |

¹ The plots M, N, Q, and T were not included in this average.

SERIES I

Definite quantities of glycocoll and leucine were thoroughly mixed with 50 gm. portions of soil, and kept in covered tumblers at room temperature ranging from 22 to 27° C. In the present series, like in the others, the soil used had about 18 per cent moisture. Care was also taken to replace the loss in weight through evaporation by periodical addition of distilled water which was previously boiled and cooled. At the end of six days contents of the tumblers were distilled with magnesium oxide in the case of leucine, and with barium carbonate, in the case of glycocoll, since it was found that glycocoll, when mixed with soil and subjected without delay to distillation with magnesium oxide, splits off a small portion of its nitrogen in the form of ammonia. This is also true of some of the other amino acids or acid amides. Where this was the case, barium carbonate was used instead of magnesium oxide. In some instances the soil portions were distilled with magnesium oxide and the duplicate portions with barium carbonate. The results obtained are recorded in the following table:

| Soil No. | Amount of soil used | Amount of amino acid added | Ammonia nitrogen formed | | |
|-------------|------------------------|-------------------------------|-------------------------|---------|----------------------------------|
| | | | Amount | Average | Per cent of total nitrogen |
| 1 | 50 grams | nothing | 2.06 mg | | |
| 2 | 50 " | nothing | 2.70 " | 2.38 mg | |
| 3 | 50 " | 0.1 gr. glycocoll | 14.70 " | | |
| 4 | 50 " | 0.1 " " | 14.57 " | 14.64 " | 78.71 |
| 5 | 50 " | 0.2 " " | 30.19 " | | |
| 6 | 50 " | 0.2 " " | 29.25 " | 29.72 " | 79.89 |
| 7 | 50 " | 0.3 " " | 44.96 " | | |
| 8 | 50 " | 0.3 " " | 44.89 " | 44.93 " | 80.52 |
| 9 | 50 " | 0.4 " " | 60.02 " | | |
| 10 | 50 " | 0.4 " " | 60.56 " | 60.29 " | 81.03 |
| 11 | 50 " | 0.5 " " | 74.27 " | | |
| 12 | 50 " | 0.5 " " | 74.03 " | 74.15 " | 79.73 |
| 13 | 50 " | 0.1 gr. Leucine | 5.24 " | | |
| 14 | 50 " | 0.1 " " | 4.99 " | 5.12 " | 48.53 |
| 15 | 50 " | 0.2 " " | 10.56 " | | |
| 16 | 50 " | 0.2 " " | 10.49 " | 10.53 " | 49.81 |
| 17 | 50 " | 0.3 " " | 15.90 " | | |
| 18 | 50 " | 0.3 " " | 16.11 " | 16.01 " | 50.58 |
| 19 | 50 " | 0.5 " " | 24.60 " | | |
| 20 | 50 " | 0.5 " " | 25.59 " | 25.10 " | 47.58 |

The soil numbers 1 and 2 to which no amino acid was added, gave on distillation with magnesium oxide 2.38 mgs. ammonia nitrogen. Equally it was found that 50 grams of soil when distilled with barium carbonate yielded 0.28 mgs. ammonia nitrogen. These amounts were subtracted from the ammonia nitrogen obtained by distillation of the amino acid treated soils with magnesium oxide or barium carbonate respectively. The results were then expressed in percentage of the total nitrogen actually found in the amino acids by the Kjeldahl method.

Some eighty per cent of glycocoll nitrogen were ammonified in the same period in which about forty nine per cent of leucine nitrogen were transformed into ammonia. Since all conditions, like moisture, temperature, amount of soil, etc. were the same,

the difference between glycocoll and leucine, as far as the percentage of ammonia produced is concerned is quite striking. It seems fairly safe to ascribe the slower formation of ammonia from leucine to the inert paraffin character of the comparatively long hydrocarbon chain contained in the leucine molecule.

SERIES II

Varying amounts of leucine and phenylalanine were well mixed mixed with weighed quantities of soil and kept in beakers covered with Petri plates. The highest room temperature observed during the experiment was 26° C., the lowest 17. The soil portions 1–10, 11–30, 31–40 were distilled at the end of five, seven and ten days respectively. The results are summarized in the following table:

| Soil No. | Amount of soil used | Amount of amino acid added | Soil No. | Amount of soil used | Amount of amino acid added |
|----------|---------------------|----------------------------|----------|---------------------|----------------------------|
| 1 | 25 Grams | 0.1 gr. Leucine | 21 | 25 Grams | 0.1 gr phenylalanine |
| 2 | 25 " | 0.1 " " | 22 | 25 " | 0.1 " " |
| 3 | 50 " | 0.1 " " | 23 | 50 " | 0.1 " " |
| 4 | 50 " | 0.1 " " | 24 | 50 " | 0.1 " " |
| 5 | 75 " | 0.1 " " | 25 | 75 " | 0.1 " " |
| 6 | 75 " | 0.1 " " | 26 | 75 " | 0.1 " " |
| 7 | 100 " | 0.1 " " | 27 | 100 " | 0.1 " " |
| 8 | 100 " | 0.1 " " | 28 | 100 " | 0.1 " " |
| 9 | 125 " | 0.1 " " | 29 | 125 " | 0.1 " " |
| 10 | 125 " | 0.1 " " | 30 | 125 " | 0.1 " " |
| 11 | 25 " | 0.2 " " | 31 | 25 " | 0.2 " " |
| 12 | 25 " | 0.2 " " | 32 | 25 " | 0.2 " " |
| 13 | 50 " | 0.2 " " | 33 | 50 " | 0.2 " " |
| 14 | 50 " | 0.2 " " | 34 | 50 " | 0.2 " " |
| 15 | 75 " | 0.2 " " | 35 | 75 " | 0.2 " " |
| 16 | 75 " | 0.2 " " | 36 | 75 " | 0.2 " " |
| 17 | 100 " | 0.2 " " | 37 | 100 " | 0.2 " " |
| 18 | 100 " | 0.2 " " | 38 | 100 " | 0.2 " " |
| 19 | 125 " | 0.2 " " | 39 | 125 " | 0.2 " " |
| 20 | 125 " | 0.2 " " | 40 | 125 " | 0.2 " " |

| Soil No. | Ammonia nitrogen formed | | | Soil No. | Ammonia nitrogen formed | | |
|----------|-------------------------|---------|----------------------------|----------|-------------------------|---------|----------------------------|
| | Amount | Average | Per cent of total nitrogen | | Amount | Average | Per cent of total nitrogen |
| 1 | 2.11 mg | | | 21 | 3.85 mg | | |
| 2 | 2.74 " | 2.43 mg | 23.03 | 22 | 3.74 " | 3.80 mg | 44.86 |
| 3 | 4.68 " | | | 23 | 4.51 " | | |
| 4 | 4.57 " | 4.63 " | 43.89 | 24 | 4.09 " | 4.30 " | 50.77 |
| 5 | 5.83 " | | | 25 | 3.57 " | | |
| 6 | 5.06 " | 5.45 " | 51.66 | 26 | 3.04 " | 3.31 " | 39.08 |
| 7 | 5.88 " | | | 27 | 2.90 " | | |
| 8 | 5.76 " | 5.82 " | 55.17 | 28 | 3.39 " | 3.15 " | 37.19 |
| 9 | 6.16 " | | | 29 | 1.64 " | | |
| 10 | 6.42 " | 6.29 " | 59.62 | 30 | 2.27 " | 1.96 " | 23.14 |
| 11 | 9.34 " | | | 31 | 5.87 " | | |
| 12 | 8.57 " | 8.96 " | 42.46 | 32 | 4.56 " | 5.22 " | 30.81 |
| 13 | 10.12 " | | | 33 | 8.98 " | | |
| 14 | 9.62 " | 9.87 " | 46.78 | 34 | 8.16 " | 8.57 " | 50.59 |
| 15 | 10.89 " | | | 35 | 9.80 " | | |
| 16 | 10.54 " | 10.72 " | 50.81 | 36 | 8.59 " | 9.20 " | 54.31 |
| 17 | 11.66 " | | | 37 | 9.90 " | | |
| 18 | 11.14 " | 11.40 " | 54.03 | 38 | 6.94 " | 8.42 " | 49.70 |
| 19 | 11.98 " | | | 39 | 8.91 " | | |
| 20 | 11.94 " | 11.96 " | 56.68 | 40 | 6.66 " | 7.79 " | 45.99 |

By reference to the table we can readily see that the amount of ammonia formed increased as larger quantities of either leucine or phenylalanine were applied, but while the percentage of ammonia increased with larger amounts of soil used, in the case of leucine it was not quite pronounced, in the case of phenylalanine. Making due allowance for the rather wide variation in the proportions of ammonia obtained, we note, however, that on the whole the percentage of ammonia produced from phenylalanine in the soil was smaller than from leucine, and much less than from glycocoll. This is, since conditions were equal to be attributed to the chemical structure of phenylalanine, i. e., to the resistant character of its benzene ring which is very likely destroyed simultaneously with the deamination of its side chain.

SERIES III

Weighed amounts of asparagine and aspartic acid were thoroughly mixed with definite quantities of soil and kept in covered tumblers at room temperature ranging from 17 to 28°C. The amounts of ammonia formed in the soil numbers 1–10, 11–30, 31–40 were ascertained by distillation at the end of seven, nine and ten days respectively. The results are given in the table below.

| Soil No. | Amount of soil used | Amount of amino anid added | Soil No. | Amount of soil used | Amount of amino acid added |
|----------|---------------------|----------------------------|----------|---------------------|----------------------------|
| 1 | 50 grams | 0.1 gr. asparagine | 21 | 50 grams | 0.2 gr. asparagine |
| 2 | 50 " | 0.1 " " | 22 | 50 " | 0.2 " " |
| 3 | 75 " | 0.1 " " | 23 | 75 " | 0.2 " " |
| 4 | 75 " | 0.1 " " | 24 | 75 " | 0.2 " " |
| 5 | 100 " | 0.1 " " | 25 | 100 " | 0.2 " " |
| 6 | 100 " | 0.1 " " | 26 | 100 " | 0.2 " " |
| 7 | 125 " | 0.1 " " | 27 | 125 " | 0.2 " " |
| 8 | 125 " | 0.1 " " | 28 | 125 " | 0.2 " " |
| 9 | 150 " | 0.1 " " | 29 | 150 " | 0.2 " " |
| 10 | 150 " | 0.1 " " | 30 | 150 " | 0.2 " " |
| 11 | 50 " | 0.1 " aspartic acid | 31 | 50 " | 0.2 " aspartic acid |
| 12 | 50 " | 0.1 " " " | 32 | 50 " | 0.2 " " " |
| 13 | 75 " | 0.1 " " " | 33 | 75 " | 0.2 " " " |
| 14 | 75 " | 0.1 " " " | 34 | 75 " | 0.2 " " " |
| 15 | 100 " | 0.1 " " " | 35 | 100 " | 0.2 " " " |
| 16 | 100 " | 0.1 " " " | 36 | 100 " | 0.2 " " " |
| 17 | 125 " | 0.1 " " " | 37 | 125 " | 0.2 " " " |
| 18 | 125 " | 0.1 " " " | 38 | 125 " | 0.2 " " " |
| 19 | 150 " | 0.1 " " " | 39 | 150 " | 0.2 " " " |
| 20 | 150 " | 0.1 " " " | 40 | 150 " | 0.2 " " " |

| Soil No. | Ammonia nitrogen formed | | | Soil No. | Ammonia nitrogen formed | | |
|----------|-------------------------|----------|----------------------------|----------|-------------------------|----------|----------------------------|
| | Amount | Average | Per cent of total nitrogen | | Amount | Average | Per cent of total nitrogen |
| 1 | 14.74 mg | | | 21 | 32.52 mg | | |
| 2 | 15.73 " | 15.24 mg | 72.68 | 22 | 32.46 " | 32.49 mg | 77.47 |
| 3 | 14.74 " | | | 23 | 31.79 " | | |
| 4 | 14.37 " | 14.56 " | 69.43 | 24 | 29.44 " | 30.62 " | 72.99 |
| 5 | 15.26 " | | | 25 | 30.48 " | | |
| 6 | 13.32 " | 14.29 " | 68.14 | 26 | 26.63 " | 28.56 " | 68.10 |
| 7 | 14.32 " | | | 27 | 30.59 " | | |
| 8 | 11.91 " | 13.12 " | 62.57 | 28 | 25.01 " | 27.80 " | 66.29 |
| 9 | 13.76 " | | | 29 | 29.64 " | | |
| 10 | 11.35 " | 12.56 " | 59.90 | 30 | 23.75 " | 26.70 " | 63.64 |
| 11 | 6.93 " | | | 31 | 15.06 " | | |
| 12 | 6.82 " | 6.88 " | 64.91 | 32 | 15.20 " | 15.13 " | 71.37 |
| 13 | 7.10 " | | | 33 | 14.68 " | | |
| 14 | 7.13 " | 7.12 " | 67.17 | 34 | 14.85 " | 14.77 " | 69.67 |
| 15 | 7.24 " | | | 35 | 14.54 " | | |
| 16 | 7.41 " | 7.33 " | 69.06 | 36 | 14.47 " | 14.51 " | 68.44 |
| 17 | 7.66 " | | | 37 | 15.17 " | | |
| 18 | 7.76 " | 7.71 " | 72.74 | 38 | 15.06 " | 15.12 " | 71.32 |
| 19 | 7.80 " | | | 39 | 14.47 " | | |
| 20 | 7.14 " | 7.47 " | 70.47 | 40 | 14.36 " | 14.42 " | 68.02 |

A glance at the table shows that the amount of ammonia produced in the soil from asparagine was practically doubled as the quantity of asparagine added to the soil was doubled. This holds also good for aspartic acid. It is further interesting to note that the average percentage of ammonia produced from either asparagine or aspartic acid is about the same which is convincing proof that the agencies active in the soil are able to split off the nitrogen from the aspartic acid—a pure amino acid—as readily as they split it off from the asparagine which is at the same time an acid amide and amino acid.

SERIES IV

The amino acids tyrosine and glutamic acid mixed with weighed amounts of soil were kept in beakers covered with Petric plates at room temperature which ranged from 19 to 29 C. Contents of the beakers were distilled with magnesium oxide after the expiration of the following intervals: Soil numbers 1-8 after six days, numbers 9 to 16 as well as Nos. 25 to 32 after seven days, numbers 17-24 after eight days, numbers 33-40 after nine days, and numbers 41-48 after eleven days. The data secured are reported in the following table:

| Soil No. | Amount of soil used | Amount of amino acid added | Soil No. | Amount of soil used | Amount of amino acid added |
|----------|---------------------|----------------------------|----------|---------------------|----------------------------|
| 1 | 25 grams | 0.05 gr glutamic acid | 25 | 25 grams | 0.05 gr. tyrosine |
| 2 | 25 " | 0.05 " " " | 26 | 25 " | 0.05 " " |
| 3 | 50 " | 0.05 " " " | 27 | 50 " | 0.05 " " |
| 4 | 50 " | 0.05 " " " | 38 | 50 " | 0.05 " " |
| 5 | 100 " | 0.05 " " " | 29 | 100 " | 0.05 " " |
| 6 | 100 " | 0.05 " " " | 30 | 100 " | 0.05 " " |
| 7 | 150 " | 0.05 " " " | 31 | 150 " | 0.05 " " |
| 8 | 150 " | 0.05 " " " | 32 | 150 " | 0.05 " " |
| 9 | 25 " | 0.1 " " " | 33 | 25 " | 0.1 " " |
| 10 | 25 " | 0.1 " " " | 34 | 25 " | 0.1 " " |
| 11 | 50 " | 0.1 " " " | 35 | 50 " | 0.1 " " |
| 12 | 50 " | 0.1 " " " | 36 | 50 " | 0.1 " " |
| 13 | 100 " | 0.1 " " " | 37 | 100 " | 0.1 " " |
| 14 | 100 " | 0.1 " " " | 38 | 100 " | 0.1 " " |
| 15 | 150 " | 0.1 " " " | 39 | 150 " | 0.1 " " |
| 16 | 150 " | 0.1 " " " | 40 | 150 " | 0.1 " " |
| 17 | 25 " | 0.2 " " " | 41 | 25 " | 0.2 " " |
| 18 | 25 " | 0.2 " " " | 42 | 25 " | 0.2 " " |
| 19 | 50 " | 0.2 " " " | 43 | 50 " | 0.2 " " |
| 20 | 50 " | 0.2 " " " | 44 | 50 " | 0.2 " " |
| 21 | 100 " | 0.2 " " " | 45 | 100 " | 0.2 " " |
| 22 | 100 " | 0.2 " " " | 46 | 100 " | 0.2 " " |
| 23 | 150 " | 0.2 " " " | 47 | 150 " | 0.2 " " |
| 24 | 150 " | 0.2 " " " | 48 | 150 " | 0.2 " " |

| Soil No. | Ammonia nitrogen formed | | | Soil No. | Ammonia nitrogen formed | | |
|-------------|-------------------------|---------|--|-------------|-------------------------|---------|----------------------------------|
| | Amount | Average | Per cent of total nitro- gen | | Amount | Average | Per cent of total nitrogen |
| 1 | 2.69 mg | | | 25 | 1.70 mg | | |
| 2 | 2.71 " | 2.70 mg | 57.32 | 26 | 1.70 " | 1.70 mg | 44.04 |
| 3 | 3.25 " | 3.27 " | 69.43 | 27 | 1.77 " | | |
| 4 | 3.28 " | 3.27 " | 69.43 | 28 | 2.29 " | 2.03 " | 52.59 |
| 5 | 3.21 " | | | 29 | 2.05 " | | |
| 6 | 3.10 " | 3.16 " | 67.09 | 30 | 2.13 " | 2.09 " | 54.15 |
| 7 | 3.21 " | | | 31 | 2.20 " | | |
| 8 | 3.03 " | 3.12 " | 66.24 | 32 | 1.75 " | 1.98 " | 51.30 |
| 9 | 6.34 " | | | 33 | 4.02 " | | |
| 10 | 6.34 " | 6.34 " | 67.30 | 34 | 3.92 " | 3.97 " | 51.42 |
| 11 | 6.50 " | | | 35 | 3.95 " | | |
| 12 | 6.58 " | 6.54 " | 69.43 | 36 | 4.23 " | 4.09 " | 52.98 |
| 13 | 6.04 " | | | 37 | 3.60 " | | |
| 14 | 6.06 " | 6.05 " | 64.23 | 38 | 3.67 " | 3.64 " | 47.15 |
| 15 | 6.15 " | | | 39 | 3.81 " | | |
| 16 | 6.34 " | 6.25 " | 66.35 | 40 | 3.81 " | 3.81 " | 49.35 |
| 17 | 13.38 " | | | 41 | 9.28 " | | |
| 18 | 13.41 " | 13.40 " | 71.13 | 42 | 9.14 " | 9.21 " | 59.65 |
| 19 | 13.62 " | | | 43 | 9.11 " | | |
| 20 | 13.67 " | 13.60 " | 72.19 | 44 | 8.90 " | 9.01 " | 58.35 |
| 21 | 12.21 " | | | 45 | 7.85 " | | |
| 22 | 12.59 " | 12.40 " | 65.82 | 46 | 7.88 " | 7.87 " | 50.97 |
| 23 | 12.63 " | | | 47 | 7.88 " | | |
| 24 | 12.47 " | 12.55 " | 66.61 | 48 | 7.81 " | 7.85 " | 50.84 |

From the table we can readily see that the amount of ammonia formed was fairly proportional to the quantity of amino acid employed in the case of both glutamic acid and tyrosine. The most instructive fact which is brought out by this as well as by the previous series is the great influence of the chemical structure of the amino acids upon the rate of their ammonification. Thus, the glutamic acid which has the same structure as aspartic acid of which it is the next homologue quantitatively almost equals the aspartic acid in its ammonification. Similarly, tyrosine which has the NH₂ group in the side chain of the benzene

ring as does phenylalanine from which it differs only by one hydroxyl group, shows a comparatively low proportion of ammonification as does phenylalanine. The above being the case it is fairly safe to assume that glutamine which is the next higher homologue of asparagine, will ammonify in about the same manner as the asparagine did.

SERIES V

Alanine mixed with weighed quantities of soil was kept in covered beakers at room temperature ranging from 21 to 29° C. The distillation of soil portions 1-8 and 9-24 was carried out after nine and ten days respectively. The results secured were as follows:

| Soil No. | Amount of soil used | Amount of amino acid added | Ammoniacal nitrogen formed | | |
|-------------|---------------------------|-------------------------------|----------------------------|----------|----------------------------------|
| | | | Amount | Average | Per cent of total nitrogen |
| 1 | 25 grams | 0.1 gr. Alanine | 9.56 mg | | |
| 2 | 25 " | 0.1 " " | 11.21 " | 10.39 mg | 66.60 |
| 3 | 50 " | 0.1 " " | 9.83 " | | |
| 4 | 50 " | 0.1 " " | 9.45 " | 9.64 " | 61.80 |
| 5 | 100 " | 0.1 " " | 7.13 " | | |
| 6 | 100 " | 0.1 " " | 6.81 " | 6.97 " | 44.68 |
| 7 | 150 " | 0.1 " " | | | |
| 8 | 150 " | 0.1 " " | 8.34 " | 8.34 " | 53.46 |
| 9 | 25 " | 0.2 " " | 22.76 " | | |
| 10 | 25 " | 0.2 " " | 24.40 " | 23.58 " | 75.58 |
| 11 | 50 " | 0.2 " " | 21.42 " | | |
| 12 | 50 " | 0.2 " " | 22.23 " | 21.83 " | 69.97 |
| 13 | 100 " | 0.2 " " | 19.92 " | | |
| 14 | 100 " | 0.2 " " | 16.89 " | 18.41 " | 59.01 |
| 15 | 150 " | 0.2 " " | 19.04 " | | |
| 16 | 150 " | 0.2 " " | | 19.04 " | 61.03 |
| 17 | 25 " | 0.3 " " | 30.73 " | | |
| 18 | 25 " | 0.3 " " | 31.63 " | 31.18 " | 66.62 |
| 19 | 50 " | 0.3 " " | 34.41 " | | |
| 20 | 50 " | 0.3 " " | 35.52 " | 34.97 " | 74.72 |
| 21 | 100 " | 0.3 " " | 32.37 " | | |
| 22 | 100 " | 0.3 " " | 28.61 " | 30.49 " | 65.15 |
| 23 | 125 " | 0.3 " " | 30.35 " | | |
| 24 | 125 " | 0.3 " " | 30.35 " | 64.85 " | |

While the amounts of ammonia increased fairly proportionally to the quantities of alanine added to the soil, there does not seem to be a definite relation between the ammonia formed and the amounts of soil employed. The behavior of alanine in the soil on the whole confirms the observation already made, as to the influence of chemical structure on the intensity of transformation. Accordingly, the quantities of ammonia obtained from alanine, with the exception of but a few distillations, approach those secured from glycocoll of which alanine is the next higher homologue.

The results presented in this paper do not warrant yet conclusive deductions. In the first place the question as to whether amino acids can in the soil quantitatively be deaminized needs still further investigation. It is possible that while the ammonification of the amino acids is still going on in the soil, a part of the ammonia produced is oxidized to nitrites and nitrates. Loss of nitrogen through denitrification, as well as loss of ammonia escaping from the soil as gas is also not out of the question. Other factors will also have to be taken into consideration. However, the data at hand permit of drawing the following conclusions:

The amino acids and acid amides¹ examined readily undergo in the soil the process of ammonification.

All other things being equal, the rate of transformation of the amino acid nitrogen into ammonia is greatly influenced by the chemical structure of the amino acids so that amino acids of equal structure yield about the same proportion of ammonia and vice versa.

Under the conditions outlined in the experiments, the various amino acids yielded the following maximum proportions, ammonia:

Glycocolle, 81.03%; alanine 75.58%; leucine 59.62%; aspartic acid 72.74%; glutamic acid 72.19%; phenylalanine 54.31%; tyrosine 59.65%; asparagine 77.47%.

I wish to thank Mr. E. H. Kellogg and Mr. R. Snyder for assistance in carrying out the routine work.

¹ In addition to asparagine, also experiments concerning the ammonification of acetamide and propionamide have just been completed by the writer. They will be published in another paper.

(*Abstract*)

THE EFFECT OF LIME UPON THE ALKALI TOLERANCE OF WHEAT SEEDLINGS

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Experiments were conducted with wheat seedlings in culture mediums, in sand and in clay, the sand and clay being kept saturated with the same strength of sodium chloride as the corresponding culture mediums. In the culture solution it was found that the tolerance of the wheat seedling for sodium chloride was about .30%. In the sand the seedlings were a bit more resistant to the toxic effect of the sodium chloride, but in the clay a marked tolerance was manifested by the seedlings toward the sodium chloride. This was found to be due to the small amount of lime, which the clay contained and not to the power of absorption which the clay possessed. Analysis of the seedlings grown in .40% sodium chloride with and without the addition of calcium salt to the culture medium showed the presence of as much sodium chloride absorbed by the seedlings grown in the sodium chloride in the presence of the lime as in those grown in the sodium chloride solution only. It is apparent therefore that the benefit which lime exerts is not one of preventing the absorption of the toxic sodium chloride by the plant, but rather one in which the toxicity of the sodium chloride is overcome by the presence of the lime. Lime showed the same tendency to overcome the toxicity of sodium sulphate, although the sodium sulphate was absorbed by the plant to as great an extent in the presence of the lime as in its absence. In other words lime does not act as a dam thus preventing the absorption of injurious salts, but neutralizes any toxic action those salts may possess.

TRI-LOCAL SOIL-EXCHANGE EXPERIMENTS WITH WHEAT

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INTRODUCTION

In bulletin 128 of the Bureau of Chemistry it was shown that neither the composition of the wheat nor its physical characteristics were to any great extent hereditary; that those characteristics such as protein, gluten, ash content, etc., and the size of the berry, weight per bushel and flintiness of kernel were all dependent upon the climatic conditions prevailing during the growing period of the plant; that when wheat seed obtained from one locality, *e. g.*, Kansas (and containing 20 per cent protein and showing 100 per cent of flinty kernels) and from another locality, *e. g.*, California (containing 10 per cent of protein with 13 per cent flinty kernels) were grown side by side in any locality, *e. g.* in South Dakota, the composition and the physical appearance of the resulting crops were identical, and when they were grown side by side in California, the composition and physical properties of the two crops were likewise identical. The crops grown in California were, however, entirely different from those grown in South Dakota, due to the great divergence in climatic conditions. The data given in that bulletin (128) showed in a most conclusive manner that environment played the major part in influencing both the chemical composition and the physical appearance of a wheat crop and it was assumed that the soil played a relatively small role. The conclusion was reached that "wheat of the same variety obtained from different sources and possessing widely different chemical and physical characteristics when grown side by side in any one locality, yields crops which are almost identical in appearance and in composition." The converse was also true, viz. that "wheat of any one variety, from any one source and absolutely alike in chemical and physical char-

acteristics, when grown in different localities, possessing different climatic conditions, yield crops of very widely different appearance and very different in chemical composition." These differences were due to the environment under which these wheats grew, that is the soil, and the climatic conditions at the time of growth.

In this bulletin it is intended to show just how much influence is being exerted by soil and what part is played by the ordinary climatic conditions such as rainfall, sunshine, humidity of the atmosphere, temperature, winds, elevation above sea level, etc. taken together.

In order to distinguish between the role played by soil and that by climatic conditions, samples of soil were interchanged between three localities, differing widely in climatic conditions. These localities were College Park, Md., Hays, Kans., and Davis, Calif. From each locality sections of soil 5' square and 3' deep were transported to each of the other localities. This soil was dug up in 3" layers, sacked and replaced in the same original position in the new localities. In order to obviate any differences due to this manipulation of soil a section of soil from each locality, 5' square and 3' deep was likewise dug up in 3" layers, sacked and stored, until the soils from the other two localities had arrived when all three samples were placed in their respective positions. A further test was to determine whether the manipulation which these soils had undergone would exert any influence on the composition of the grain and therefore a fourth plot of the same size in each locality, was allowed to remain undisturbed, *i. e.*, the soil was not dug up in 3" layers, as were the other three plots. Thus, we had in each locality four small 5' square plots each 3' deep, *e. g.*, in California there was the California undisturbed plot, the California soil plot, which had been dug up in 3" layers and put back again in the same position and the Kansas soil plot and the Maryland soil plot. In Kansas there was a plot from California soil, from Maryland soil and from Kansas soil, all of which had been taken up in 3" layers and put back in their respective positions besides which there was a plot of Kansas undisturbed soil, called the check plot; the same was true in Maryland.

During the first year 1908 Crimean wheat was used. This was obtained from seed grown in Kansas. This seed was used for the next year's crop 1909 on each of the four plots in each of the three localities. Owing to the fact that Crimean wheat was not adapted to conditions prevailing in Maryland and California it was decided thereafter to use Turkey wheat, and therefore for 1910 and continuing throughout 1911 Turkey wheat was used. The change from Crimean to Turkey does not interfere, however with the object of the experiment which is to determine what influence climatic conditions and soil respectively exert upon the composition of the crop because in each locality and in each soil the same variety of wheat was used. The following determinations were made, water, weight per 1000, weight per bushel, flinty grains, nitrogen, alcohol soluble nitrogen, fat fiber, pentosans, sugars, ash, phosphoric acid and potash. These determinations were made according to the methods published in Bureau of Chemistry Bulletin 107. The alcohol soluble nitrogen was determined by treating a certain amount of ground wheat with 70 per cent alcohol at ordinary temperature with frequent shaking for several hours and then allowing the solution to stand over night. An aliquot was taken and the nitrogen determined therein. The amount of nitrogen thus obtained, divided by the total nitrogen in the sample gave the gliadin ratio. Tables numbered 1, 2, 3 and 4 give the results obtained on all the samples beginning with the original sample, the analysis of which is found in Table 1. In Table 5 the same data are rearranged, bringing together in adjacent columns results from the same soils. In Tables 6, 7 and 8 are given the average, minimum, and maximum results of analyses from the wheats grown in the different localities and those grown on different soils, besides a comparison of results obtained from the check plots with the corresponding soil which had been taken up in 3" layers.

In 1909 (see Table 2) the crop in Kansas was a complete failure. We had, therefore, only the four samples from California and the three samples from Maryland, no sample from the check plot having been harvested in Maryland that year. The weight per thousand kernels of the samples grown in California on the four different soils varied very largely, the Maryland soil producing

wheat considerably smaller than the wheat grown on the other three soils. The weight per 1000 of these latter three samples was about the same. In Maryland, however, there was no appreciable difference in the weight per thousand in the wheats grown on the California, Kansas or Maryland soil. A considerable difference was noted in the percentage of nitrogen in the wheats grown on the four soils in California, the wheat from both Maryland and Kansas being relatively low in nitrogen, while those grown on the California soil both in the regular plot and in the undisturbed plot were rather high. That this peculiarity was not due entirely to the difference in soil may be seen by consulting Table 3, that is the crop of 1910, where it is noted that the wheat grown in California on the Maryland soil was the highest in nitrogen while those grown in California on both the California check and the normal soil plot, were much lower. Again referring to Table 2, or the 1909 crop, it is noted that there is no great difference in the percentage of nitrogen in the three samples of wheat grown on the three soils in Maryland, showing in this case that it is not the soil which influences mostly the composition of plants. Comparing the gliadin ratio a general uniformity is noted in all the samples. That grown on the Maryland soil in California seems to be somewhat low in gliadin content, while the one from the California check plot is correspondingly high. There is no great difference in the fat content of the four samples grown in California nor in the three samples grown in Maryland, except that the latter are uniformly higher than the former. The same similarity is noted regarding the fiber, pentosans and ash, while in the case of the sugars the samples grown in Maryland are somewhat lower than those in California. The phosphoric acid and potash in the ash of the samples of wheat grown in California are also quite uniform in amount. The same is true of those grown in Maryland. While the P_2O_5 in the ash of the four samples grown in California is more or less similar and that of the samples of wheat grown in Maryland are also more or less similar, there is nevertheless quite a difference between the composition of the samples grown in Maryland and those grown in California, the former containing appreciably more P_2O_5 in the ash than do the latter. All the Maryland samples are much

higher in ash and in the amount of phosphoric acid which the ash contains than are the samples grown in California. A remarkable uniformity exists in the amount of potash in the ash. No appreciable difference is apparent in the K₂O content of the ash whether the samples were grown on the four different soils in California or in Maryland. Referring to Table 3 which gives the results of the 1910 crop we have here four samples grown in California, four grown in Kansas and three in Maryland. With the exception of the difference in the nitrogen content previously noted, and in the weight per thousand kernels in the sample of wheat grown in California on the Maryland soil, there seems to be no great differences in the composition of the four samples grown in California on the four different soils when considered by themselves or on the four samples grown in Kansas on the four different soils when considered by themselves, and likewise with the three samples grown in Maryland. There is, however, a very great difference between the percentage composition of the grains grown in California, Kansas and Maryland, the Kansas samples being as a rule lower in weight per thousand and higher in the percentage of nitrogen and protein. Again there is noted a very great uniformity in the gliadin ratio of all the samples whether they were grown in California, Kansas or in Maryland. The same applies to the amount of potash in the ash. It is again noted that the phosphoric acid in the ash of the samples grown in Maryland is appreciably higher than the phosphoric acid in the ash in either the samples grown in Kansas or California. The samples grown in California are lower in fiber content and in ash than those grown in Kansas or Maryland. With the exception of one sample, that grown in Maryland soil, the wheats grown in California are likewise lower in pentosans than those grown in Kansas or Maryland. The California samples, are, however, higher in sugar content than those from Kansas or Maryland. The same was true in 1909. Another interesting point to be noted is that the grain grown in California varied from 70 to 100 per cent flinty while those in Maryland showed no completely flinty grains, while those grown in Kansas were entirely flinty. This important point emphasizes once more the small rôle played by the soil in influencing the physical appear-

ance of wheat. Looking at it in another way, the wheat grown on Maryland soil in Maryland contained 0 flinty grains, on Maryland soil in Kansas 100 flinty, on Maryland soil in California likewise 100 flinty grains.

Table 4 gives the results of the 1911 crop. In this case there was a complete failure in California, no crop being obtained. However, here we have the four samples grown in Kansas, and the four in Maryland. Here again is noted a very great uniformity in the composition of the four samples grown in Kansas, irrespective of the source of the soil. A similar uniformity exists among the samples grown in Maryland but when the Kansas samples are compared with the Maryland samples it is at once noted that the weight per thousand of the Kansas samples are about one-half of those grown in Maryland and the percentage of nitrogen in the samples grown in Kansas are almost double that of the samples grown in Maryland. The fiber, pentosans and ash content of the Kansas-grown samples are appreciably higher than the corresponding constituents made on the Maryland-grown samples. There is one exception to this and that is the ash of the wheat grown on the Maryland soil in Kansas which for some unexplained reason is much lower than the ash of the other three samples of wheat grown in Kansas. Again we note that the phosphoric acid of the ash of the wheat grown in Maryland is much higher than that of the ash of the samples grown in Kansas. This has been noted during 1909 and 1910 also. Just why Maryland wheat is composed of a greater amount of phosphoric acid containing ash is unexplained for no analysis or study was made of the soil *per se*.

There is no appreciable difference in the fat content nor in the amount of potash in the ash between the Kansas or Maryland grown samples irrespective of the source of the soil.

The Kansas grown samples are practically 100 per cent flinty, while those grown in Maryland are less than half flinty. To show, once more, that soil has much less influence upon the appearance and chemical composition of wheat the following is given: the Kansas soil plot in Kansas produced a wheat containing 23.3 per cent protein, 2.94 per cent fiber, 9.12 pentosans, 2.56 ash and 46 per cent of P_2O_5 in the ash, while wheat on the Kansas soil

plot in Maryland contained only 12.5 per cent protein, 2.33 fiber, 8.22 pentosans, 2.20 ash, but contained 53 per cent P₂O₅ in the ash. The weight per 1000 of the former is 13.3 g., of the latter, 29.4, while the flinty grains are 98 and 20 per cent respectively. Similar differences are to be noted between the crops grown on the California soil in Kansas and that in Maryland, and likewise between the crops grown on the Maryland soil plot in Kansas and that in Maryland.

Table 5 contains the same figures as are found in Table 2, 3, and 4 but arranged according to the source of the soil. In this table one can easily note the effect of environment upon the composition and physical characteristics of the crop, the factor of soil being entirely eliminated. Thus great differences are seen in the composition of the wheat when grown on the same kind of soil, but in different localities. This is especially true between samples grown in Kansas and Maryland, or Kansas and California. No such differences are noted between Maryland and California grown samples, because the climatic conditions between these two localities are more nearly alike than are those of either one of them with California.

Table 6 gives the resumé of Tables 2, 3, 4, the figures being arranged according to the locality irrespective of the source of the soil. For example the figures show the average, minimum and maximum determinations of all the samples grown in California, averaged by themselves, also in Kansas and in Maryland. In this table it is seen that it is the climatic conditions which influence to a great extent both the physical characteristics and the chemical composition of wheat. This was brought out in bulletin 128 already mentioned. Taking only the average figures we find that the California grown samples weigh most per thousand grains and the Kansas samples weigh the least. The Maryland samples have the least number of flinty grains, the Kansas samples have the most. The California samples and the Maryland samples are more or less similar in the average percentage composition while the samples grown in Kansas are much higher in nitrogen than the wheats grown in the other two states. There is no appreciable difference in the fat, pentosans, and sugar of the samples grown in the three states. The wheats grown in Kansas

are appreciably higher in fiber than those grown in California or Maryland. This is due to the fact that the weight per thousand was smaller in Kansas. The ash of the California samples is somewhat lower than the ash of the Kansas or Maryland grown samples. There is a very general agreement in the gliadin ratio and in the potash content of the average of all samples of wheat whether grown in California, Kansas or Maryland. Regarding the phosphoric acid in the ash, the samples grown in Maryland average much higher than those grown in California or Kansas. This table shows in general that the composition of wheat and its appearance depend upon the conditions prevailing during the growing period in the different localities. In Table 7 averages minimum and maximum are taken from Tables 2, 3, 4 and 5 and arranged according to the source of soil for example all samples grown on the California soils whether these California soils be in California, Kansas or Maryland are averaged together, likewise all the samples grown on Kansas and on Maryland soils respectively. From this table it is apparent, when the averages only are considered, that there is no appreciable difference, either in the physical appearance or in the chemical composition of the grains. In other words it makes no appreciable difference in the composition of wheat whether a wheat is grown on Maryland soil, on Kansas soil or on California soil when all three soils are in one locality. These figures would seem to show that the influence which soil exerts on the physical appearance and the composition of the grain is a very small factor, indeed, and that most of the differences found in the appearance and the composition of wheat is due directly to the climatic conditions existing during the time the wheats were grown. A glance at Table 7 will show that there is no appreciable difference in the weight per thousand, weight per bushel or the flinty characters of the grain nor in the percentage of protein or the gliadin ratio, fat, fiber, pentosans, sugars or ash, likewise the amount of phosphoric acid and potash in the ash are very constant. Table 8 affords a comparison between the data obtained on the wheat grown on the soil which had been taken up in 3" layers and replaced in the same order and those on wheat which had been grown on the adjacent check plots. The conclusions to be drawn from this table are virtually but

a verification of the conclusions already drawn from Table 7 wherein it has been shown that the soil exerts practically no influence on the composition of the grain, for in Table 8 we see that not only is the physical appearance of the grain practically the same but there is no appreciable difference in the chemical composition due to the handling of the soil.

GENERAL SUMMARY

This work has been carried on for three years; with very few exceptions it has been found that wheat grown in one locality on soils obtained from different sources and at great distances show great similarity in composition, establishing the fact that soil in these experiments plays only a minor part in affecting either the physical appearance or chemical composition of wheat.

On the other hand when wheat is grown on the same soil which has been transported from one locality to others of decidedly different climatic conditions the composition of the wheat varies very greatly. This is most clearly shown in Table 3 for 1910 showing that it is the climatic conditions which affect both the appearance and composition of plants.

TABLE I.—TRILOCAL SOIL EXCHANGE EXPERIMENTS—
CRIMEAN WHEAT—1908 CROP

| | Original seed grown in Kansas |
|---|----------------------------------|
| Water..... | 9.20 |
| Wt. per 1,000..... | 26.3 |
| Wt. per bushel..... | 57.7 |
| Flinty grains..... | —p |
| <i>On Water Free Basis</i> | |
| Nitrogen..... | 2.58 |
| Protein (N x 5.7)..... | 14.75 |
| Alc. sol. nitrogen..... | 1.03 |
| Gliadin ratio..... | 40 |
| Fat..... | — |
| Fiber..... | — |
| Pentosans..... | 8.70 |
| Sugars..... | 2.52 |
| Ash..... | 2.05 |
| Phosphoric acid..... | 0.96 |
| Potash..... | 0.55 |
| P ₂ O ₅ in ash..... | 46 |
| K ₂ O in ash..... | 25 |

II.—TRILOCAL SOIL EXCHANGE EXPERIMENTS—CRIMEAN WHEAT 1909 CROP

| | Wheat Grown in California on | | | | Wheat Grown in Kansas on | | | | Wheat Grown in Maryland on | | | |
|--------------------|------------------------------|----------------|--------------|-------------|--------------------------|--------------|-----------------------|-------------|----------------------------|--------------|-------------|----------------------|
| | Calif. check soil | Calif. soil | Kan. soil | Md. soil | Calif. soil | Kan. soil | Kan. check soil | Md. soil | Calif. soil | Kan. soil | Md. soil | Md. check soil |
| Water..... | 9.64 | 8.98 | 9.00 | 8.88 | | | | | 9.56 | 9.48 | 9.22 | |
| Wt. per 1000..... | 36.2 | 34.6 | 36.4 | 25.4 | | | | | 21.2 | 23.0 | 22.2 | |
| Wt. per bu..... | 62.7 | 61.5 | 61.5 | | | | | | | | | |
| Flinty grains..... | 100 | 100 | 75. | 97. | | | | | 85p | 80p | -ss | |

On Water Free Basis

| | | | | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Nitrogen..... | 2.59 | 2.78 | 2.01 | 2.03 | | | | | 2.69 | 2.57 | 2.34 | |
| Protein (N x 5.7)..... | 14.76 | 15.84 | 11.46 | 11.57 | | | | | 15.33 | 14.65 | 13.34 | |
| Alc. sol. N..... | 1.23 | 1.16 | 0.82 | 0.71 | | | | | 1.10 | 1.05 | 0.92 | |
| Gliadin ratio..... | 46 | 41 | 41 | 35 | | | | | 41 | 41 | 40 | |
| Fat..... | 1.67 | 1.82 | 1.82 | 1.84 | | | | | 2.16 | 2.05 | 2.15 | |
| Fiber..... | 2.18 | 2.33 | 2.43 | 2.39 | | | | | 2.69 | 2.62 | 2.59 | |
| Pentosans..... | 8.22 | 8.49 | 8.16 | 8.53 | | | | | 8.37 | 8.31 | 9.03 | |
| Sugars..... | 3.53 | 3.21 | 3.73 | 3.26 | | | | | 2.89 | 2.64 | 2.82 | |
| Ash..... | 1.72 | 1.63 | 1.63 | 1.90 | | | | | 2.39 | 2.30 | 2.09 | |
| Phosphoric acid..... | .79 | 0.68 | 0.70 | 0.89 | | | | | 1.23 | 1.18 | | |
| Potash..... | 0.48 | 0.45 | 0.46 | 0.56 | | | | | | 0.63 | | |
| P ₂ O ₅ in ash..... | 46 | 42 | 43 | 47 | | | | | 51 | 51 | | |
| K ₂ O in ash..... | 28 | 28 | 29 | 30 | | | | | 27 | | | |

III.—TRILOCAL SOIL EXCHANGE EXPERIMENTS—TURKEY WHEAT 1910 CROP

| | Wheat Grown in California on | | | | Wheat Grown in Kansas on | | | | Wheat Grown in Maryland on | | | |
|--------------------------|------------------------------|----------------|--------------|-------------|--------------------------|--------------|-----------------------|-------------|----------------------------|--------------|-------------|----------------------|
| | Calif. check soil | Calif. soil | Kan. soil | Md. soil | Calif. soil | Kan. soil | Kan. check soil | Md. soil | Calif. soil | Kan. soil | Md. soil | Md. check soil |
| Water..... | 9.81 | 9.68 | 9.67 | 8.99 | 9.39 | 9.03 | 9.30 | 9.12 | 9.00 | 10.66 | 9.73 | |
| Wt. per 1,000 grain..... | 31.2 | 28.3 | 34.3 | 21.5 | 26.1 | 22.6 | 23.3 | 24.0 | 28.0 | 31.5 | 25.9 | |
| Wt. per bushel..... | 60.5 | | 61.8 | | 58.3 | 56.9 | 57.2 | 55.8 | | 57.7 | | |
| Flinty grains..... | 99p | 100p | 70p | 100ss | 99 | 100ss | 100ss | 100ss | Op. | Op. | Op. | |

On Water Free Basis

| | | | | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Nitrogen..... | 2.16 | 2.39 | 1.86 | 2.86 | 2.80 | 3.28 | 3.23 | 3.12 | 1.80 | 1.90 | 2.04 | |
| Protein (N x 5.7)..... | 12.31 | 13.63 | 10.60 | 16.28 | 15.98 | 18.73 | 18.41 | 17.81 | 10.27 | 10.85 | 11.68 | |
| Alc. sol. nitrogen..... | .96 | 1.05 | 0.74 | | 1.23 | 1.44 | 1.32 | 1.29 | | 0.75 | | |
| Gliadin ratio..... | 44 | 44 | 40 | | 44 | 41 | 41 | 41 | | 39 | | |
| Fat..... | 2.01 | 2.13 | 2.13 | 2.11 | 1.86 | 2.04 | 1.81 | 2.02 | 1.67 | 1.76 | 1.78 | |
| Fiber..... | 2.26 | 2.15 | 2.28 | 2.35 | 2.72 | 2.79 | 2.78 | 2.80 | 2.65 | 3.01 | 2.63 | |
| Pentosans..... | 8.27 | 8.32 | 8.57 | 0.25 | 8.64 | 8.93 | 8.78 | 8.64 | 8.70 | 8.54 | 8.84 | |
| Sugars..... | 3.40 | 3.53 | 3.81 | 3.43 | 3.13 | 3.38 | 3.11 | 3.33 | 2.90 | 2.99 | 3.06 | |
| Ash..... | 1.87 | 1.84 | 1.82 | 2.05 | 1.99 | 1.97 | 2.29 | 1.97 | 2.09 | 2.07 | 2.22 | |
| Phosphoric acid .. | 0.84 | 0.79 | 0.86 | 1.02 | 0.85 | 0.81 | 1.08 | 0.80 | | 1.09 | 1.21 | |
| Potash..... | 0.60 | 0.61 | 0.55 | 0.65 | 0.61 | 0.66 | 0.69 | 0.64 | | 0.57 | 0.61 | |
| P ₂ O ₅ in ash..... | 45 | 43 | 47 | 50 | 43 | 41 | 47 | 41 | | 53 | 59 | |
| K ₂ O in ash..... | 32 | 33 | 30 | 28 | 31 | 31 | 30 | 30 | | 28 | 27 | |

IV.—TRILOCAL SOIL EXCHANGE EXPERIMENTS—TURKEY WHEAT 1911 CROP

| | Wheat Grown in California on | | | | Wheat Grown in Kansas on | | | | Wheat Grown in Maryland on | | | |
|---------------------|------------------------------|----------------|--------------|-------------|--------------------------|--------------|-----------------------|-------------|----------------------------|--------------|-------------|----------------------|
| | Calif. check soil | Calif. soil | Kan. soil | Md. soil | Calif. soil | Kan. soil | Kan. check soil | Md. soil | Calif. soil | Kan. soil | Md. soil | Md. check soil |
| Water..... | | | | | 9.00 | 9.30 | 8.28 | 8.79 | 8.83 | 8.97 | 8.93 | 8.73 |
| Wt. per 1,000..... | | | | | 12.9 | 13.3 | 12.5 | 13.8 | 27.4 | 29.4 | 27.1 | 26.4 |
| Wt. per bushel..... | | | | | | | | | 60.5 | 62.2 | | 59.9 |
| Flinty grains..... | | | | | 100ss | 98ss | 97ss | 98ss | 25p | 20p | —p | 50p |

On Water Free Basis

| | | | | | | | | | | | | |
|---|--|--|--|--|-------|-------|-------|-------|-------|-------|-------|-------|
| Nitrogen..... | | | | | 3.70 | 4.09 | 4.07 | 3.97 | 2.00 | 2.20 | 2.37 | 2.31 |
| Protein (N x 5.7)..... | | | | | 21.11 | 23.31 | 23.18 | 22.62 | 11.38 | 12.52 | 13.52 | 13.18 |
| Alr. sol. Nitrogen..... | | | | | | | | | 0.85 | 0.88 | 1.04 | 0.96 |
| Gliadin ratio..... | | | | | | | | | 43 | 40 | 44 | 41 |
| Fat..... | | | | | 1.94 | 1.95 | 1.83 | 2.12 | 2.04 | 2.05 | 1.83 | 1.87 |
| Fiber..... | | | | | 2.95 | 2.94 | 3.17 | 3.21 | 2.41 | 2.33 | 2.49 | 2.44 |
| Pentosans..... | | | | | 8.84 | 9.12 | 9.57 | 9.12 | 8.08 | 8.22 | 8.25 | 8.39 |
| Sugars..... | | | | | | | | | 3.25 | 3.45 | 3.33 | 3.34 |
| Ash..... | | | | | 2.58 | 2.56 | 2.78 | 2.09 | 2.23 | 2.20 | 2.10 | 2.17 |
| Phosphoric acid..... | | | | | 1.14 | 1.18 | | 0.86 | 1.24 | 1.16 | 1.09 | 1.17 |
| Potash..... | | | | | 0.69 | | | 0.64 | 0.67 | 0.65 | 0.65 | 0.67 |
| P ₂ O ₅ in ash..... | | | | | 44 | 46 | | 41 | 56 | 53 | 52 | 54 |
| K ₂ O in ash..... | | | | | 27 | | | 30 | 30 | 30 | 31 | 31 |

V.—TRILOCAL EXCHANGE EXPERIMENTS 1909 TO 1911, ARRANGED ACCORDING TO SOURCE OF SOIL

| | 1909 Wheat grown on | | | | | | 1910 Wheat grown on | | | | | | 1911 Wheat grown on | | | | | | | | | |
|---------------------------------------|-----------------------|-------|-------|-------------------|-------|-------|---------------------|-------|-------|-----------------------|-------|-------|---------------------|-------|-------|---------------------|-------|-------|-------|-------|-------|------|
| | California soil in | | | Kansas soil in | | | Maryland soil in | | | California soil in | | | Kansas soil in | | | Maryland soil in | | | | | | |
| | Calif. | Kan. | Md. | Calif. | Kan. | Md. | Calif. | Kan. | Md. | Calif. | Kan. | Md. | Calif. | Kan. | Md. | Calif. | Kan. | Md. | | | | |
| Water. | 8.98 | 9.56 | 9.00 | 9.48 | 8.88 | 9.22 | 9.68 | 9.39 | 9.00 | 9.67 | 9.03 | 10.66 | 8.99 | 9.12 | 9.73 | 9.00 | 8.83 | 9.30 | 8.97 | 8.79 | 8.93 | |
| Wt. per 1000 grains | 34.6 | 21.2 | 36.4 | 23.0 | 25.4 | 22.2 | 28.3 | 26.1 | 28.0 | 34.3 | 22.6 | 31.5 | 21.5 | 24.0 | 25.9 | 12.9 | 27.4 | 13.3 | 29.4 | 13.8 | 27.1 | |
| Wt. per bu. | 61.5 | 36.5 | 61.5 | 55.3 | 58.3 | 58.3 | 61.8 | 56.9 | 57.7 | 55.8 | 60.5 | 60.5 | 60.5 | 60.5 | 60.5 | 60.5 | 100ss | 100ss | 100ss | 100ss | 100ss | |
| Flinty grains | 100 | 85 | 75 | 80 | 97 | 99 | 100p | 99 | 99 | 100p | 100ss | 100ss | 100ss | 100ss | 100ss | 100ss | 100ss | 100ss | 100ss | 100ss | 100ss | |
| <i>On Water Free Basis</i> | | | | | | | | | | | | | | | | | | | | | | |
| Nitrogen. | 2.78 | 2.69 | 2.01 | 2.57 | 2.03 | 2.34 | 2.39 | 2.80 | 1.80 | 1.86 | 3.28 | 1.90 | 2.86 | 3.12 | 2.04 | 3.70 | 2.00 | 4.09 | 2.20 | 3.97 | 2.37 | |
| Protein (N x 5.7) | 15.84 | 15.33 | 11.46 | 14.65 | 11.57 | 13.34 | 13.63 | 15.98 | 10.27 | 10.60 | 18.73 | 10.85 | 16.28 | 17.81 | 11.68 | 21.11 | 11.38 | 23.31 | 12.52 | 22.62 | 13.52 | |
| Alc. sol. nitrogen | 1.16 | 1.05 | 0.82 | 1.05 | 0.71 | 0.92 | 1.047 | 1.23 | 0.738 | 1.44 | 0.754 | 1.29 | 0.854 | 1.054 | 0.879 | 1.041 | 0.879 | 1.041 | 1.041 | 1.041 | 1.041 | |
| Gliadin ratio. | 41 | 41 | 41 | 41 | 35 | 40 | 44 | 44 | 40 | 41 | 39 | 41 | 39 | 41 | 41 | 43 | 40 | 40 | 40 | 40 | 44 | |
| Fat. | 1.82 | 2.16 | 1.82 | 2.05 | 1.84 | 2.15 | 2.13 | 1.86 | 1.67 | 2.13 | 2.04 | 1.76 | 2.11 | 2.02 | 1.78 | 1.94 | 2.04 | 1.94 | 2.05 | 2.12 | 1.83 | |
| Fiber. | 2.33 | 2.69 | 2.43 | 2.62 | 2.39 | 2.59 | 2.15 | 2.72 | 2.65 | 2.28 | 2.79 | 3.01 | 2.35 | 2.80 | 2.63 | 2.95 | 2.41 | 2.95 | 2.33 | 3.21 | 2.49 | |
| Pentosans | 8.49 | 8.37 | 8.16 | 8.31 | 8.53 | 9.03 | 8.32 | 8.64 | 8.70 | 8.57 | 8.93 | 8.54 | 9.25 | 8.64 | 8.84 | 8.08 | 8.84 | 8.22 | 9.12 | 8.25 | 9.12 | |
| Sugars. | 3.21 | 2.89 | 3.73 | 2.64 | 3.26 | 2.82 | 5.53 | 3.13 | 2.90 | 3.81 | 3.38 | 2.99 | 3.43 | 3.33 | 3.06 | 3.25 | 3.25 | 3.45 | 3.25 | 3.33 | 3.33 | |
| Ash. | 1.63 | 2.39 | 1.63 | 2.30 | 1.90 | 2.09 | 1.84 | 1.99 | 2.09 | 1.82 | 1.97 | 2.07 | 2.05 | 1.97 | 2.22 | 2.58 | 2.23 | 2.58 | 2.20 | 2.09 | 2.10 | |
| Phosphoric acid. | 0.68 | 1.23 | .70 | 1.18 | .89 | 0.79 | 0.86 | 0.79 | 0.86 | 0.61 | 0.55 | 0.66 | 0.57 | 0.65 | 0.64 | 0.61 | 0.69 | 0.67 | 1.14 | 1.16 | 0.86 | 1.09 |
| Potash. | .45 | .51 | .43 | .46 | .63 | .56 | .61 | .61 | .43 | .47 | .41 | .53 | .50 | .41 | .59 | .44 | .56 | .44 | .53 | .41 | .52 | |
| P ₂ O ₅ in ash. | 42 | 51 | 43 | 51 | 47 | 30 | 33 | 31 | 31 | 30 | 28 | 30 | 27 | 30 | 27 | 30 | 27 | 30 | 27 | 30 | 31 | |
| K ₂ O in ash. | 28 | 28 | 29 | 29 | 27 | 30 | 33 | 31 | 31 | 30 | 31 | 31 | 30 | 31 | 30 | 31 | 30 | 31 | 30 | 31 | 31 | |

VI.—TRILOCAL SOIL EXCHANGE EXPERIMENT WITH WHEAT—TABLE OF AVERAGES AND EXTREMES BY LOCALITY¹

WHEAT GROWN ON THE THREE SOILS IN

| | California | | | Kansas | | | Maryland | | |
|---------------------|------------|--------|-------|---------|--------|-------|----------|--------|-------|
| | Average | Minim- | Maxi- | Average | Minim- | Maxi- | Average | Minim- | Maxi- |
| Water..... | 9.03 | 8.88 | 9.68 | 9.10 | 8.79 | 9.39 | 9.37 | 8.83 | 10.66 |
| Wt. per 1,000..... | 30.1 | 21.5 | 36.4 | 18.8 | 12.9 | 26.1 | 26.2 | 21.2 | 31.5 |
| Wt. per bushel..... | 61.6 | 61.5 | 61.8 | 57.1 | 55.8 | 58.3 | 60.0 | 57.7 | 62.2 |
| Flinty grains..... | 88 | 70 | 100 | 99 | 99 | 100 | 31 | 0 | 85 |

On Water Free Basis]

| | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Nitrogen..... | 2.32 | 1.86 | 2.86 | 3.49 | 2.80 | 4.09 | 2.21 | 1.80 | 2.69 |
| Protein (N x 5.7)..... | 13.22 | 10.60 | 16.28 | 19.86 | 15.98 | 23.31 | 12.61 | 10.27 | 15.33 |
| Alc. sol. nitrogen..... | .89 | .71 | 1.16 | 1.32 | 1.23 | 1.44 | .94 | .75 | 1.10 |
| Gliadin ratio..... | 41 | 35 | 44 | 42 | 44 | 41 | 41 | 39 | 43 |
| Fat..... | 1.98 | 1.82 | 2.13 | 2.00 | 1.86 | 2.04 | 1.95 | 1.67 | 2.16 |
| Fiber..... | 2.33 | 2.15 | 2.43 | 2.90 | 2.72 | 3.21 | 2.58 | 2.33 | 3.01 |
| Pentosans..... | 8.56 | 8.16 | 9.25 | 8.88 | 8.64 | 9.12 | 8.48 | 8.08 | 9.03 |
| Sugars..... | 3.48 | 3.21 | 3.81 | 3.28 | 3.13 | 3.38 | 3.04 | 2.64 | 3.45 |
| Ash..... | 1.82 | 1.63 | 2.32 | 2.19 | 1.97 | 2.58 | 2.19 | 2.07 | 2.39 |
| Phosphoric acid..... | .82 | .68 | 1.01 | .94 | .80 | 1.18 | 1.21 | 1.09 | 1.54 |
| Potash..... | .54 | .46 | .65 | .64 | .61 | .69 | .64 | .57 | .67 |
| P ₂ O ₅ in ash..... | 45 | 42 | 47 | 43 | 41 | 46 | 53 | 51 | 59 |
| K ₂ O in ash..... | 30 | 28 | 33 | 30 | 27 | 31 | 29 | 27 | 31 |

¹ Not including check plots.

VII.—TRILOCAL SOIL EXCHANGE EXPERIMENT WITH WHEAT—TABLE OF AVERAGES AND EXTREMES

BY SOURCE OF SOIL¹

Wheat Grown in the Three Localities on

| | California Soil | | | Kansas Soil | | | Maryland Soil | | |
|---------------------|-----------------|--------|-------|-------------|--------|-------|---------------|--------|--------|
| | Average | Minim- | Maxi- | Average | Minim- | Maxi- | Average | Minim- | Maxi- |
| Water..... | 9.20 | 8.83 | 9.68 | 9.44 | 8.97 | 10.65 | 9.09 | 8.79 | 9.73 |
| Wt. per 1,000..... | 26.9 | 12.9 | 34.6 | 27.2 | 13.3 | 36.4 | 22.8 | 13.8 | 27.1 |
| Wt. per bushel..... | 60.1 | 58.3 | 61.5 | 60.6 | 57.7 | 62.2 | only | one | sample |
| Flinty grains..... | 73 | 0 | 100 | 63 | 0 | 100 | 79 | 0 | 100 |

On Water Free Basis

| | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Nitrogen..... | 2.59 | 1.80 | 3.70 | 2.56 | 1.90 | 4.09 | 2.68 | 2.03 | 3.97 |
| Protein (N x 5.7)..... | 14.79 | 10.27 | 21.11 | 14.68 | 10.85 | 23.31 | 15.26 | 11.57 | 22.62 |
| Alc. sol. nitrogen..... | 1.08 | .85 | 1.23 | .95 | .74 | 1.44 | .99 | .71 | 1.29 |
| Gliadin ratio..... | 43 | 41 | 44 | 40 | 39 | 41 | 40 | 35 | 44 |
| Fat..... | 1.95 | 1.67 | 2.16 | 1.97 | 1.76 | 2.13 | 1.98 | 1.78 | 2.15 |
| Fiber..... | 2.56 | 2.15 | 2.95 | 2.63 | 2.28 | 3.01 | 2.63 | 2.35 | 3.21 |
| Pentosans..... | 8.49 | 8.08 | 8.84 | 8.55 | 8.16 | 9.12 | 8.81 | 8.25 | 9.25 |
| Sugars..... | 3.15 | 2.89 | 3.53 | 3.33 | 2.64 | 3.81 | 3.20 | 2.82 | 3.43 |
| Ash..... | 2.11 | 1.63 | 2.58 | 2.08 | 1.63 | 2.56 | 2.05 | 1.90 | 2.22 |
| Phosphoric acid..... | 0.99 | .68 | 1.24 | .99 | .70 | 1.18 | .96 | .80 | 1.21 |
| Potash..... | .61 | .45 | .69 | .59 | .46 | .66 | .62 | .56 | .65 |
| P ₂ O ₅ in ash..... | 47 | 42 | 56 | 48 | 41 | 53 | 48 | 41 | 59 |
| K ₂ O in ash..... | 30 | 27 | 33 | 29 | 27 | 31 | 29 | 27 | 31 |

¹ Not including check plots.

VIII.—TRILOCAL SOIL EXCHANGE EXPERIMENT WITH WHEAT—TABLE OF AVERAGES AND EXTREMES

| | Condition of Soil | | | | | |
|--------------------------------------|-------------------|--------|-------|-------------|--------|-------|
| | Disturbed | | | Undisturbed | | |
| | Average | Minim- | Maxi- | Average | Minim- | Maxi- |
| Water..... | 9.18 | 8.93 | 9.30 | 9.15 | 8.28 | 9.81 |
| Wt. per 1,000..... | 25.1 | 13.3 | 34.6 | 25.9 | 12.5 | 36.2 |
| Wt. per bushel (only 2 samples)..... | | | | 60.0 | 57.2 | 62.7 |
| Flinty grains..... | 100 | 98 | 100 | 89 | 50 | 100 |

On Water Free Basis

| | | | | | | |
|---------------------------------|-------|-------|-------|-------|-------|-------|
| Nitrogen..... | 2.98 | 2.37 | 4.09 | 2.87 | 2.16 | 4.07 |
| Protein ($N \times 5.7$)..... | 17.06 | 13.52 | 23.31 | 16.37 | 12.31 | 23.18 |
| Ale. sol. nitrogen..... | 1.17 | 1.04 | 1.44 | 1.12 | .96 | 1.32 |
| Gliadin ratio..... | 43. | 41. | 44. | 43. | 41. | 46. |
| Fat..... | 1.91 | 1.82 | 2.13 | 1.84 | 1.67 | 2.01 |
| Fiber..... | 2.54 | 2.15 | 2.94 | 2.57 | 2.18 | 3.17 |
| Pentosans..... | 8.62 | 8.25 | 9.12 | 8.65 | 8.22 | 9.57 |
| Sugars..... | 3.36 | 3.21 | 3.53 | 3.34 | 3.11 | 3.53 |
| Ash..... | 2.12 | 1.63 | 2.58 | 2.17 | 1.72 | 2.78 |
| Phosphoric acid..... | .84 | .68 | 1.09 | .97 | .79 | 1.17 |
| Potash..... | .59 | .45 | .66 | .61 | .48 | .69 |
| P_2O_5 in ash..... | 44 | 38 | 52 | 48 | 45 | 54 |
| K_2O in ash..... | 31 | 28 | 33 | 30 | 28 | 32 |

(Abstract)

FACTORS RELATING TO THE AVAILABILITY OF NITROGENOUS PLANT-FOODS

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The decomposition of organic matter is influenced by factors which may be designated as external and internal. The external factors as moisture, aeration, etc., are more readily modified than the internal factors, such as the mechanical and chemical composition of the organic substances used. The experimental work here reported deals with both the external and internal factors as they relate to the availability of nitrogenous substances. All the experiments were carried out in glazed earthenware jars or painted earthenware pots, and pure quartz sand was used in all cases, except in Series 2, which was a study of the influence of the mechanical composition of the soil on the availability of nitrogen in organic compounds. In nearly all cases the crop grown was barley.

Tests were conducted to determine the optimum moisture content for crops grown under control in pure quartz sand. Four sets of pots were employed, maintaining the moisture at $4\frac{3}{4}$, 7, 9 and 11 per cent. In each set three nitrogenous fertilizing materials were used, viz: nitrate of soda, dried blood and cottonseed meal. It was found that the highest percentage of nitrogen was recovered where the moisture was maintained at 9 per cent, though with 11 per cent, the amount recovered was nearly as great. The pots that received nitrate of soda gave the largest yield of dry matter, and also the largest yield of nitrogen. In these pots the proportion of nitrogen was lower with the larger amounts of water.

In studying the influence of the mechanical composition of the soil on the availability of nitrogenous organic compounds,

sand and red shale soil were used, both separated, and in varying combinations. In this work it was found that the per cent of nitrogen in the dry matter decreased as the percentage of sand was increased; this was likewise true of portions to which alfalfa meal and cow manure were added. As the proportion of sand was increased there was a decrease in the weight of dry matter produced, but this decrease was not proportional to the decrease in the amount of nitrogen in the mixture.

We, therefore, find a great increase in the percentage of nitrogen recovered from the mixtures of sand and soil up to 50 per cent of sand. This is probably due to the more complete oxidation of the organic matter of the soil, brought about by the improved physical condition. However, when quantities of alfalfa meal and cow manure were added to the mixture the reverse was almost invariably true, that is, the percentage of nitrogen recovered decreased with the increase in percentage of sand.

Two explanations seem possible; either the decomposition of the organic matter was in some way checked with increased amounts of sand, or some of the nitrogen that was made available, in the decomposition processes, escaped into the air. The former view does not seem reasonable, inasmuch as determinations of nitrogen and carbon in the mixtures show a decrease in the percentage of both these elements at the end of the experiment, after due allowance has been made for the nitrogen removed in the crop. We are, therefore, forced to the conclusion that there was a heavy loss of nitrogen as gas, or as ammonia or both; not only where alfalfa meal and manure were used, but even with the mixture of sand and soil alone, and that this loss generally increased with increased percentages of sand up to 50 per cent sand. It thus appears that the loss of nitrogen in open sand soils may be considerable, due to the rapid oxidation of organic nitrogenous materials. The percentage of nitrogen recovered from organic matter, in the form of alfalfa meal, was distinctly greater than that recovered from the organic matter of either the manure or the shale soil. This is probably explained on the ground that the nitrogen of the alfalfa meal is in a more readily available form than that in either of the other materials. This seems to further emphasize the superior-

ity of green manure crops over stable manure. Taken all together the proportion of nitrogen to carbon in the soil at the end of the experiment was less than at the beginning.

In a study of the availability of the nitrogen of nitrate of soda it was shown that with applications of nitrate from one to five grams per pot, the percentage of nitrogen in the dry matter gradually increased, the amount ranging from about one per cent with the smaller applications, to nearly three and one half per cent with the 5 gram applications. There was also a gradual increase in the percentage of nitrogen recovered with applications up to three grams. Greater quantities resulted in a depressed yield of dry matter and consequently a lower percentage recovery. Attention is called to the fact that an increased protein content is desirable in some instances, as in the case of feeding materials, while in others as corn and barley for brewing and distilling, it is undesirable. Hence, in the use of nitrate of soda, the character of the crop and its subsequent utilization should to some extent determine the amount to be used.

In a series of pots so arranged as to allow a comparison of the influence of varying amounts of mineral fertilizers, it was shown that where 20 pounds of quartz sand were used, one gram of nitrate of soda, with what is termed the single portion of minerals (2 grams acid phosphate, 1 gram of K Cl or K_2SO_4 , 5 grams chalk, 0.5 gram Mg SO₄ and 0.25 gram of Fe 2(SO₄)₃) give a percentage recovery essentially as great as was given with a double portion of minerals, and this combination gave a higher recovery than was obtained with 2 grams of nitrate of soda and the double portion of minerals.

Results obtained from some experiments, planned to show the influence of nitrate of soda and sulphate of ammonia on the availability of nitrogen in dried blood, peat and leather, indicate that the salts do not have any marked effect on the availability of the nitrogen in the organic materials. In some cases their presence seemed to stimulate the decomposition of the organic matter, while in others, a depressing effect was noted.

In a series of pots in which carbohydrates (dextrose and saccharose) were used in connection with nitrate of soda, sulphate of ammonia and dried blood it was shown that the yield

of nitrogen decreased as the carbohydrate was increased. With one exception less hydrogen was recovered from pots where saccharose was used than from corresponding pots where destrose was used. It is believed that the greatly increased number of bacteria directly attributable to the presence of large quantities of carbohydrates, used a portion of the ammonia and nitrate nitrogen for the building of bacterial protein. As a result a smaller quantity of available nitrogen was left at the disposal of the plants. It is also possible that large quantities of carbohydrates may exert a direct depressing effect on growing vegetation.

In a series of pots so arranged as to allow a comparison availability of the nitrogen in dried blood and tankage with that of nitrate of soda and sulphate of ammonia, it was shown that the highest yield of nitrogen was from the nitrate of soda; the sulphate of ammonia, blood and tankage follow in the order named. In the case of the organic materials the highest recovery was usually from the highest grade materials.

The following comparison of percentages of nitrogen recovered in experiments, carried out in 1910 with those of 1911 is of interest.

| | 1910 | 1911 |
|----------------------------------|----------------------------|-------|
| Nitrate of Soda | 77.97 | 54.30 |
| Sulphate of ammonia | 66.95 | 47.20 |
| Dried blood (aver. of 8 samples) | 40.31 (Aver. of 5 samples) | 36.10 |
| Tankage (" " 10 " ") | 28.71 (" " " ") | 28.98 |

In this connection it is noted that this is the order in which nitrogen was recovered from nitrate of Soda, Sulphate of ammonia and dried blood in a ten year period where four different crops were grown in cylinders; and also in a series of experiments conducted at the Darmstadt Experiment Station, Germany.

In a series of experiments using mixed fertilizers, containing organic nitrogenous materials it was found that the recovery of organic nitrogen was usually greater from those samples having the highest percentage of organic nitrogen. This is in accord with results from blood and tankage already noted.

Tables of results are given in connection with all the series.

(Abstract)

A STUDY OF THE COMPOSITION OF BEEF FAT AS
INFLUENCED BY AGE AND CONDITION OF THE
ANIMAL AND LOCATION IN THE BODY

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For the purpose of studying the influence of age and condition upon the composition of the fat, samples of adipose tissue were selected from a number of beef steers that were slaughtered at the Missouri Agricultural Experiment Station. The animals had been fed in three groups: (1) On full feed. (2) Fed for maximum growth without the laying on of fat. (3) Fed for restricted growth. For the preliminary study the samples used were from the oldest and the youngest of each group. Samples from other animals confirmed the results as obtained from the first six.

The adipose tissue was analyzed for moisture fat and protein. Saponification value, iodine number and melting point were determined on the rendered fat.

The following conclusions were drawn:

1. The percentage of fat present in the adipose tissue varies with the location of that tissue in the animal body.
2. The percentage of fat in adipose tissue increases from outside to inside while the percentage of moisture and protein decreases.
3. For animals on the same plane of nutrition, age produces an increase of fat and a corresponding decrease of moisture in the adipose tissue.
4. In the adipose tissue a high percentage of fat is accompanied by a low percentage of moisture and protein and is indicative of the degree of fatness of the animal.
5. A high percentage of moisture and protein is accompanied by a low percentage of fat.
6. The iodine value of the fat from the fatty tissue of an animal

increases with the age and the degree of fatness of the animal while the melting point decreases with almost the same uniformity.

7. The iodine value of the fat increases from inside to outside of the body while the melting point falls in almost the same ratio.

8. The age or degree of fatness of the animal does not appear to effect the saponification value of the fat.

9. The position of the fat in the body does not appear to effect the saponification value of the fat.

(Abstract)

A STUDY OF THE COST OF MAINTENANCE AND
GROWTH AND OF THE CHANGES IN THE COM-
POSITION OF THE MATURE BEEF ANIMAL
DURING THE FATTENING PERIOD

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DESCRIPTION OF ANIMALS STUDIED

The steers used in this experiment, Nos. 18, 121, 48, 164, 197 and 588, belonged to our Regular Maintenance Cattle. The first four had previously been used in a cooperative feeding experiment, the first three being discarded on account of their poor showing. Steer No. 48 was subject to bad colds, was frequently off feed, and was a tuberculosis suspect. Steer No. 164 was a coarse boned ridgeling of late maturity but strong and thrifty. The remaining two animals had been fed as show steers. An open shed with a series of small lots was used for housing the steers.

Steers No. 18, No. 121 and No. 48 were grade Shorthorns. Steer No. 164 was a grade Hereford, steer No. 588 was a registered Angus and steer No. 197 was a registered Shorthorn. Steers No. 18 and No. 121 were calved in the spring of 1905, steer No. 48 in the spring of 1904, steer No. 164 about April 1, 1906, steer No. 588 on December 10, 1904, and steer No. 197 on October 26, 1906.

These animals were fed grain and hay at night and grain in the morning. The hay was good quality alfalfa and the grain was composed of corn chop and linseed meal in the ratio of eight to one. Water and salt were given ad libitum. From the beginning of the experiment, February 1, 1907, they were fed sufficient to maintain body weight without appreciable gain or loss. Steer No. 121, No. 48 and No. 164 were changed to a full

fed ration on July 11, 1907, June 30, 1907, and June 10, 1909, respectively. Steer No. 18 was slaughtered on November 12, 1907; Steer No. 121 was slaughtered December 11, 1907; Steer No. 48 on January 18, 1909; Steer No. 164 on November 8, 1909; Steer No. 588 on June 30, 1910; and Steer No. 197 on January 3, 1910.

Daily records were kept of all feed consumed and refused and of the weights of the steers. The feeds were analyzed as per the Official Methods of the A. O. A. C. (U. S. Dept. of Agr., Bureau of Chem., Bull. No. 107 rev., pp. 38-56).

The animals were killed with a killing hammer and then bled. Records were kept of the weights of all parts and organs, and great care was used to assure no loss or error. The regular slaughter house separations of the carcass were made as practiced by the western packers. The internal organs were composited into various systems and analyzed. The cuts of meat were separated into lean, fat, and bone by hand and were later composited. The carcass was hung two days between slaughtering and cutting, and the right half was used for all weights and analyses.

All samples were well ground and mixed in power grinders and samples were sent to the chemical laboratory and started upon immediate analysis.

Moisture (H_2O) was determined by the vacuum desiccator method, using S. and S. extraction shells and glass tubes filled partly with fat free absorbent cotton. *Fat* was extracted from the dried cones with ether in Soxhlet extractors and the cones were dried again in vacuo. *Nitrogen* was determined by the modified Kjeldahl-Gunning method. The *Protein* was calculated by multiplying the nitrogen by the factor 6.25. *Ash* was determined on ten to fifteen gram samples in crucibles over Fletcher burners after drying. *Phosphorus* was run on the ash residue, using strong hydrochloric and some nitric acid. The gravimetric method employing precipitation with both ammonium phospho-molybdate and magnesia mixture was used. All analyses were made in triplicate weighing out the sample by difference from glass stoppered weighing bottles. With bone samples it was necessary to use large samples and determine

moisture and fat on these. The residue was finely ground and analyzed as above.

SUMMARIES OF RESULTS

Maintenance Costs

1. The equations $T_{1000} = T_a \sqrt{\left(\frac{1000}{a}\right)^2}$ and

$$P_{1000} = K \text{ plus } \frac{\text{Weight} - 250}{2500}$$

are given as mathematical expressions of Armsby's maintenance requirements in therms of energy and pounds of digestible protein per day for steers of different weights. It is proposed to use the equations to calculate the requirements at one thousand pounds of a steer put on experiment at some other weight. The second formula applies between the weights 250 and 1250 pounds.

2. The maintenance requirement per thousand pounds for steers is shown to vary with six animals from 8.15 pounds of grain and 3.55 pounds of hay to 5.32 pounds of grain and 2.15 pounds of hay according to the individual. The requirements of total protein, carbohydrates, and fat are shown to be near to the Wolff-Lehmann standards. The requirement expressed as digestible protein and therms of energy varies from 0.892 pounds and 7.90 therms to 0.683 pounds and 5.404 therms. It averages 0.789 pounds of digestible protein and 6.815 therms of energy as compared to 0.5 pounds and 6 to 6.2 therms proposed by Armsby.

3. The cost above maintenance of a pound of gain is found to be 3.34 pounds of grain and 1.21 pounds of hay, or 0.388 pounds of digestible protein and 3.344 therms.

4. A marked decrease of maintenance cost is shown during maturation and after some time on a low plane of nutrition.

5. The seasons are shown to effect the cost of maintenance. It is highest in the cold winter months and lowest in the spring and early summer. It increases during very hot weather and decreases again during the fall.

Percentage Composition

6. The blood, skeleton, nervous system, and digestive and excretory system are constant in composition in so far as shown by these animals. Other animals of this experiment show a relation between moisture content of the blood and condition of the steer.

7. The hide, circulatory and nervous systems, lean flesh and fatty tissue in carcass and offal show increasing percentage of dry substance and fat with increasing fatness of the steer.

Relation of Parts to Total

8. The hide, skeleton, heart, spleen and brain and spinal cord form relatively less of the total animal as it increases in weight and fatness. The blood, nervous system, and total digestive and excretory system remain constant. The offal and kidney fat, lungs and windpipe, stomach, intestines, liver and gall, pancreas and kidney form an increasing part of the total animal as it increases in weight and fatness—goes from a low to a high plane of nutrition. On the same plane of nutrition the per cent of total may decrease with increasing weight of animal. The skeleton and lean muscle form a decreasing part of the animal as it fattens. The fatty tissue forms a greatly increasing part.

9. The head, feet, shin, shank, neck and round decrease proportionately as the animal fattens. The chuck and rump remain about constant. The loin, rib, plate, flank, and kidney fat and kidney increase proportionately.

10. The skeleton contains 84 to 90% of all the ash and phosphorous; one-third to one-twentieth of the other constituents.

11. A steer is from 19 to 42 per cent fat. One-fourth to one-twentieth of all the fat is in the skeleton, fifty to sixty-five per cent in the fatty tissue, and twelve to twenty-four per cent in the offal and kidney fat.

12. Carcass is 68 to 69 per cent of the empty animal. The "fill" is eleven per cent.

Composition of Increase

13. Increase from thin to medium condition is one-third water, one-half fat and less than one-eighth protein. Increase from

thin to very fat is one-fourth water, sixty per cent fat and less than one-twelfth protein. Increase from medium to very fat is two-thirds fat and four per cent protein.

14. A steer may store up 60 per cent of the energy consumed above maintenance in the tissue laid on the body.

(Abstract)

NEW METHOD OF DETECTING VITALITY OF SEEDS

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With an apparatus which can detect and estimate CO₂ as small as one 10 millionth of a gram, I have observed that a dry seed gives definite CO₂ as long as it is alive—quite contrary to a popular notion. Waller has discovered that living seed responds to electrical stimulation as long as it is alive. By that he came to the conclusion that even though there is no applicable chemical change, yet its vitality is expressed by its excitability.

In the study of metabolism of nerve fibre, I have observed that any tissue when stimulated gives off more CO₂, as long as it respires. Thus living seeds when stimulated give off more CO₂. With the remarkably simple method of stimulation namely crushing or injuring the seeds by rough rods, I can observe large increase of CO₂ from seeds as long as they are alive.

When I take 2 seeds of wheat of the same weights, and put one in one chamber and the other crushed in the chamber of my apparatus (see Biochemical section), you can detect from the latter large increase of CO₂ production. These experiments were tried in Lincoln oats, wheats under different conditions, both normal, and other conditions which we know will kill the plant tissue or suspends metabolic activities such as subjecting them to 60° or in ether.

We may add that this relation between CO₂ production and excitability is universal as far as my studies went in all of animal and plant tissues, provided there is no other stimulation applied.

(Résumé)

L'INFLUENCE DE L'ELEKTRICITÉ STATIQUE SUR LE DÉVELOPPEMENT, LA RÉCOLTE ET LA COM- POSITION DE LA BETTERAVE A'SUCRE

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Pour la campagne 1911 nous avons pu constater les faits suivant:

1. L'élévation de la production de matière organique sur les lots exposés à l'effluve est indéniable et s'évalue à environ 20 p. c. pour les racines et les feuillages de la betterave.

2. L'emploi d'engrais chimiques n'a pas modifié les récoltes trouvées pour les betteraves soumises à l'action de l'effluve et celles qui s'étaient développées sans l'influence de l'électricité.

3. La composition des betteraves (racines, têtes, feuilles) pendant la végétation et après la récolte est sensiblement différente pour les betteraves traitées à l'électricité et ordinaires, ce qui démontre d'une façon évidente que l'action de l'électricité statique entrait en jeu, malgré les conditions peu favorables de la campagne passée.

4. L'explication de ces effets est loin d'être simple. Ni une transpiration augmentée (Gassner), ni une excitation de la plante, ni enfin l'influence de l'électricité sur les réactions chimiques qui ont lieu lors de l'assimilation (Loeb)—réactions dans lesquelles l'action de la décharge obscure se ferait sentir (Berthelot)—ne suffisant pas à l'expliquer complètement.

On peut en effet supposer avec le même droit que l'électricité n'exerce aucune influence sur la plante elle-même, mais qu'elle agit uniquement sur le sol, en y provoquant des changements d'ordre purement chimique ou physique ou enfin d'ordre biochimique. Il est d'ailleurs possible que tous ses effets se cumulent et superposent.

C'est ce qu'il faudra résoudre par de nouveaux essais, déjà mis en marche par l'auteur de cette communication.

THE FACTORS CONDITIONING THE VELOCITY OF DISINFECTION

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The foundations of study of disinfection were laid by the work of Pasteur and Lister when these masters demonstrated that the influence of certain preservatives lay in preventing growth of putrefactive bacteria on the one hand and of disease organisms on the other. Their work was subsequently amplified by many investigations on similar lines. A great advance was, however, made by Robert Koch (1886), who was the first to institute systematic experiments with pure cultures of bacteria; by means of his "thread" method, using anthrax spores as test organism, he made a comparative study of all the known disinfectants, among which he devoted special study to the remarkable disinfectant properties of the salts of mercury.

The first occasion on which the principles and accurate quantitative methods of the chemist were applied to the study of disinfection was in 1897, when Krönig and Paul published their classic researches on disinfectants and disinfection thereby raising the subject to a higher plane of scientific enquiry than it had previously occupied. For example, they first called attention to the connection between disinfectant action and electrolytic dissociation in the case of many metallic salts, alkalies and acids.¹ They also estimated relative germicidal power by a comparison of disinfection-rate in the various cases, and by means of their garnet method, using anthrax spores as test organism, they were able to form an estimate of the initial number of bacteria present and of the survivors from time to time when exposed to the action of various germicides. They thus showed that disinfection was a gradual process, depending for any particular germicide upon

¹ The work in this direction was later made complete by the researches of Winslow and Lockridge (1906).

the temperature and the concentration of the latter, but they made no further use of their results in formulating a theory of disinfection.

On further examination, however, of the valuable series of data given by Krönig and Paul, disinfection is discovered to be an orderly time process for if numbers of surviving bacteria as ordinates are plotted against time as abscissae, the experimental points lie upon fairly smoothed curves.

The form of these curves suggested the existence of a logarithmic relation between the two variables, time on the one hand, and the number of surviving bacteria on the other. In fact the curves appeared to be very similar in form to that expressing the course of a so-called "uni-molecular reaction" and the equation

$$-\frac{dC}{dt} = KC,$$

$$\text{or } \frac{1}{t_2 - t_1} \log \frac{C_1}{C_2} = K, \text{ a constant}$$

was found to be applicable to the case of disinfection, if, in place of the terms C_1 and C_2 expressing concentration of reacting substance, numbers of surviving bacteria were inserted, thus

$$\frac{1}{t_2 - t_1} \log \frac{n_1}{n_2} = K$$

Where n_1 and n_2 are the numbers of bacteria surviving after times t_1 and t_2 respectively.

Madsen and Nyman (1907) working simultaneously with myself but independently, also discovered the existence of the above relationship from Krönig and Paul's results and, using the method of the latter, verified the law for the destruction of anthrax spores by hot water.

In the course of my own work (1908 and 1910), I was able to confirm the logarithmic nature of the disinfection process for vegetative organisms as well as spores, using a variety of germicides, including heat. In the present paper I propose to give the results of a few typical experiments as examples and then to proceed to a discussion of the probable explanation of the above relationship.

EXPERIMENTAL

The "garnet" method of Krönig and Paul, in which the organisms are presented to the disinfectant as a film dried upon the surface of a garnet, is unsuitable where vegetative bacteria are concerned. In my own experiments, therefore, this method was abandoned in favour of a modification of the "drop" method of Rideal and Walker (1903). A suitable small measured quantity of a diluted broth culture (24 hours at 37°C) of the organism under examination (or of a heated emulsion from an old agar culture in case of anthrax spores) was added to a measured quantity of disinfectant solution, placed in a thermostat at the required temperature. At definite intervals of time measured samples were withdrawn by means of special capillary pipettes fixed into the mouth of the disinfection tubes and immediately plated on gelatine or agar. The numbers of colonies were counted after incubation for 4–5 days at 20° C, or 2 days at 37°C respectively.

The exact details of the method employed, and the modifications in case of disinfection by means of hot water, as well as of the expedients adopted to secure constancy of resistance in the test organisms will be found in the references given above.

Table Ia gives the results of an experiment with anthrax spores and phenol at 33.3°C. In the case of this material (which had been previously freed from vegetative forms by heating to 80°C for ten minutes) disinfection proceeded with almost mathematical precision as a "reaction of the first order," Table Ib contains the results of an experiment of Krönig and Paul with anthrax spores and mercuric chloride for comparison. In the last column of each Table are given the values of the velocity constant, calculated on the assumption that disinfection-rate is always proportional to the concentration of surviving bacteria; the values obtained show very fair constancy.

TABLE I a.

Disinfection of Anthrax Spores with 5% phenol at 33.3°C.

(See H. C. (1908), Table II, p. 99.)

| Time minutes $=t$ | Mean number of bacteria surviving in one drop of dis- infection mixture, $=N$ | $\log_{10} N$ | $*K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$ |
|-------------------------|--|---------------|---|
| 0 = t_0 | 439 = N_0 | 2.642 | — |
| 30 | 275.5 | 2.439 | .0068 |
| 75 | 137.5 | 2.138 | .0067 |
| 120 | 46 | 1.663 | .0082 |
| 180 | 15.8 | 1.199 | .0080 |
| 246 | 5.45 | .736 | .0077 |
| 300 | 3.6 | .556 | .0069 |
| 420 | 0.5 | -.301 | .0070 |

* In this and all subsequent tables, values of K from the expression $\frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$ are calculated with Briggs' logarithms in place of natural logarithms.

TABLE I b.

Disinfection of Anthrax Spores with 0.11% mercuric chloride at 18°C.

(See Krönig and Paul (1897), Table IX, p. 26.)

| Time, minutes $=t$ | Mean number of bacteria surviving $=N$ | $\log_{10} N$ | $K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$ |
|--------------------------|--|---------------|--|
| 10 = t_0 | 2027 = N_0 | 3.307 | — |
| 15 | 672 | 2.827 | .096 |
| 20 | 564 | 2.751 | .056 |
| 25 | 382 | 2.582 | .048 |
| 30 | 251 | 2.400 | .045 |
| 35 | 179 | 2.253 | .042 |
| 40 | 138 | 2.140 | .039 |
| 45 | 101 | 2.004 | .037 |
| 50 | 80 | 1.903 | .035 |
| 60 | 39 | 1.591 | .034 |
| 70 | 6 | .778 | .042 |
| 80 | 3 | .477 | .040 |

This logarithmic relationship can also be expressed graphically; if the logarithms of concentrations of surviving bacteria as ordinates be plotted against time as abscissae, the experimental points will be found to be upon straight lines. (See Figures 1 and 1b on page 172.)

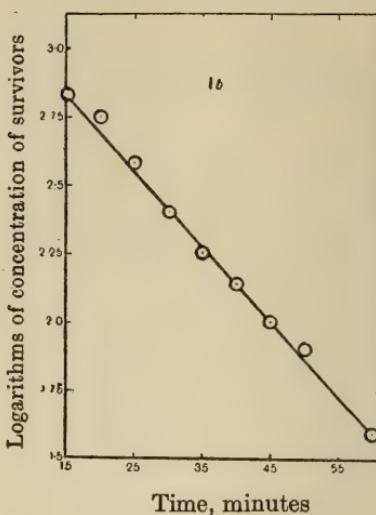
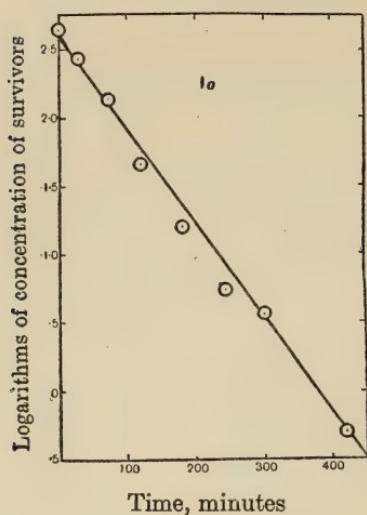


Fig. 1. (a) Disinfection of anthrax spores with 5% phenol at 33.3°C. (See Table 1a above).

(b) Disinfection of anthrax spores with 0.11% mercuric chloride at 18°C. (See Table 1b above).

Similar results were obtained for disinfection with Phenol of *B. typhosus* and *B. coli commune*: the results of a typical experiment with the former organism are shown in Table II and fig. 2 on page 173.

TABLE II.
(H. C. 1910 Table II)
*Disinfection of *B. typhosus* with 0.6% phenol at 20°C.*
EXP. 8. 1. '10.

| Time, minutes $=t$ | Amount of sample taken, drops | Numbers on plates (gelatine) | Mean | Mean no. of bacteria present in 1 drop disinfection mixture, = N | $\log_{10} N$ | $K =$ $\frac{1}{t_n - t_0}$ $\log \frac{N_0}{N_n}$ |
|--------------------------|--|------------------------------------|-------|--|---------------|--|
| 0.5 = t_0 | 1 | 236 218 240 | 231.3 | 231.3 = N_0 | 2.364 | — |
| 1.5 | 1 | 188 215 167 | 190 | 190 | 2.279 | .085 |
| 2.6 | 1 | 160 157 184 | 167 | 167 | 2.223 | .067 |
| 4.6 | 2 | 215 242 | 228.5 | 114.2 | 2.058 | .075 |
| 6.6 | 2 | 139 172 156 | 155.7 | 77.8 | 1.891 | .077 |
| 10.5 | 3 | 100 93 91 | 94.7 | 31.6 | 1.500 | .086 |
| 15 | 3 | 33 26 43 | 34 | 11.3 | 1.053 | .090 |
| 20 | 5 | 14 14 8 | 12 | 2.4 | .380 | .102 |
| 30 | 10 | 4 3 | 3.5 | .35 | -.456 | .096 |
| Mean | | | | | | .086 |

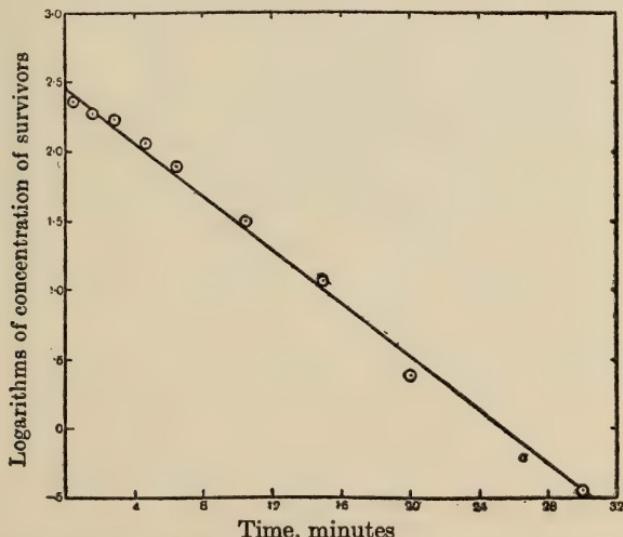


Fig. 2. Disinfection of *B. typhosus* with 0.6% phenol at 20°C. (a) Exp. 8. 1. '10, Table II.

In the case of *Staphylococcus pyogenes aureus* there was a short period (4 minutes in case of 0.6% phenol at 20° C) at the beginning of disinfection, after which disinfection conformed to the usual type and proceeded as a "reaction of the first order" (see Table III and fig. 3).

TABLE III.
(H. C., 1910, Table VI)

Disinfection of Staphylococcus pyogenes aureus with 0.6% phenol at 20° C.

EXP. 6. 4. '09.

| Time, minutes $=t$ | Amount of sample taken, drops | Numbers counted on plates (agar) | Mean | Mean no. of bacteria present in 1 drop disinfection mixture, = N | $\log_{10} N$ | $K =$ $\frac{1}{\ln t - \ln t_0}$ $\log \frac{N}{N_0}$ |
|--------------------------|---|---|--------|--|---------------|--|
| Control | 1 | 1369 1218 | 1293 | 1293 | 3.112 | — |
| 1 | 1 | 1160 1120 1143 | 1141 | 1141 | 3.057 | — |
| 3 | 1 | 974 1064 1093 | 1044 | 1044 | 3.019 | — |
| 4 = t_0 | 1 | 986 929 940 | 952 | 952 = N_0 | 2.979 | — |
| 5 | 1 | 693 669 762 | 708 | 708 | 2.850 | .129 |
| 6 | 2 | 1062 1048 1148 | 1086 | 543 | 2.735 | .122 |
| 7 | 3 | 1253 1167 1187 | 1202 | 401 | 2.603 | .125 |
| 8 | 3 | 728 731 | 729.5 | 243.2 | 2.386 | .148 |
| 9 | 5 | 1113 912 | 1012.5 | 202.5 | 2.306 | .135 |
| 10 | 5 | 761 691 890 | 780.7 | 156.1 | 2.193 | .131 |
| 12 | 10 | 626 326 410 | 454 | 45.4 | 1.657 | .165 |
| 15 | 10 | 220 216 | 218 | 21.8 | 1.338 | .149 |

Mean .136

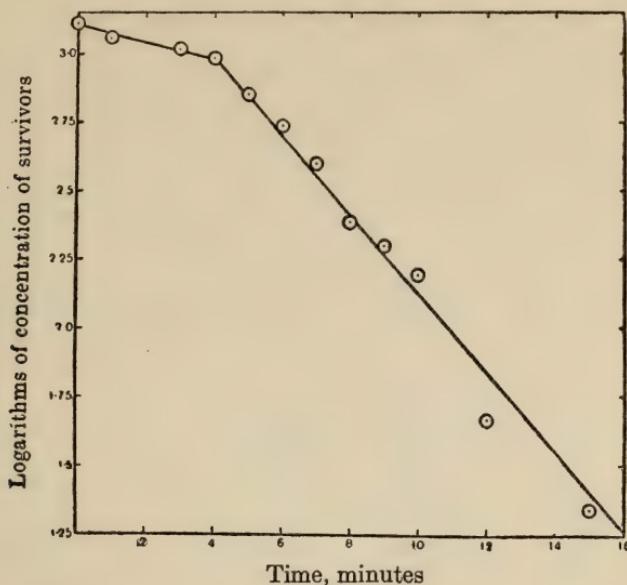


Fig. 3. Disinfection of *Staphylococcus pyogenes aureus* with 0.6% phenol at 20°C. (Exp. 6. 4. '09, Table III.)

Disinfection of *B. paratyphosus*, whether by metallic salts phenol, or other coal-tar derivatives was somewhat irregular; the reaction velocity fell off more rapidly as disinfection proceeded than it should have done if proportional only to the concentration of survivors. This point will be referred to later. (See p. 189.) The results at experiment with mercuric chloride are given in Table IV, as an example.

TABLE IV. (Exp. 23. 3. 07. H. C. 1908, Table X)

B. parat. Mercuric chloride, 2 per million. 20°C.

| Time minutes | Mean no. of bacteria present in diluted sample | | Mean no. of bacteria present in 1 drop disinfection mixture | K , assuming reaction to be in accordance with the equation $\frac{dn}{dt} = Kn$ |
|-----------------|--|------|---|--|
| 1.1 | 85 | ×250 | 21,250, taken as initial value of $n (= n_1)$ in calculating values of K | |
| 2.1 | 82 | ×250 | 20,500 | * |
| 3 | 68 | ×250 | 17,000 | * |
| 4 | 52 | ×250 | 13,000 | 0.074 |
| 5 | 53 | ×250 | 13,250 | 0.050 |
| 7 | 62 | ×250 | 15,500 | 0.023 |
| 10 | 97 | ×125 | 12,125 | 0.027 |
| 15 | 96 | ×125 | 12,000 | 0.017 |
| 20 | 69 | ×100 | 6,900 | 0.026 |
| 30 | 139 | ×50 | 6,950 | 0.018 |
| 42 | 305 | ×25 | 7,625 | 0.011 |
| 51 | 279 | ×25 | 6,975 | 0.010 |
| 60 | 276 | ×10 | 2,760 | 0.015 |
| 80 | 215 | ×10 | 2,150 | 0.012 |
| 93 | 130 | ×10 | 1,300 | 0.013 |
| 140 | — | — | 150 | 0.015 |
| 180 | — | — | 49 | 0.015 |
| 210 | — | — | 29 | 0.013 |
| 245 | — | — | 29 | 0.012 |

* The values of n at these times are not sufficiently accurate to give consistent values for K .

Disinfection by hot water.

Disinfection by hot water proceeded as a "unimolecular" reaction in the case of *B. typhosus*, *B. coli commune*, and *B. pestis*. In the case of *Staphylococcus pyogenes aureus* and *B. paratyphosus* some irregularity was again displayed at the beginning of the disinfection, which afterwards proceeded in the usual manner. The results of two experiments with *B. coli commune* at two different temperatures are given below, as examples. (See Table V and fig. 4.)

TABLE V. (H. C. 1910., Table XII)
Disinfection of B. coli commune with hot water.

EXP. I, 15. 2. '10. Temperature 48.9°C.

| Time, minutes $=t$ | Amount of sample taken, drops | Numbers counted on plates (agar) | Mean | Mean no. of bacteria present in 1 drop disinfection mixture, $=N$ | $\log_{10} N$ | $K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$ |
|--------------------------|---|---|------------|---|---------------|--|
| 0.25 = t_0 | 1 | 371 362 383 | 372 | 372 = N_0 | 2.570 | — |
| 1.0 | 1 | 266 253 304 | 274.3 | 274.3 | 2.438 | .176 |
| 2 | 1 | 191 178 201 | 190 | 190 | 2.279 | .166 |
| 4 | { 1 2 | 68 76 129 | — } — } | 68.25 | 1.834 | .196 |
| 6 | { 1 2 | 25 44 | — } — } | 23 | 1.362 | .210 |
| 10 | { 2 5 | 16 29 67 | — } — } | 12.4 | 1.093 | .152 |
| 15 | { 5 10 | 10 15 18 | — } — } | 1.72 | .235 | .159 |
| 20 | { 10 20 | 1 6 10 | — } — } | .425 | -.372 | .149 |
| | | | | | Mean | .172 |

EXP. II, 15. 2. '10. Temperature 52.7°C.

| | | | | | | |
|--------------|----------|-------------|------------|-------------|--------|------|
| 0.25 = t_0 | 1 | 416 331 402 | 383 | 383 = N_0 | 2.583 | — |
| 1.0 | 1 | 207 235 183 | 208 | 208 | 2.318 | .353 |
| 2 | 1 | 93 73 103 | 89.7 | 89.7 | 1.953 | .360 |
| 4 | 2 | 21 47 19 | 29 | 14.5 | 1.161 | .379 |
| 6 | { 3 5 | 4 3 5 | — } — } | 1.1 | .041 | .442 |
| 8 | 10 | 6 5 | 5.5 | .55 | -.260 | .367 |
| 10 | 10 | 1 0 1 | .66 | .066 | -1.181 | .386 |
| | | | | | Mean | .381 |

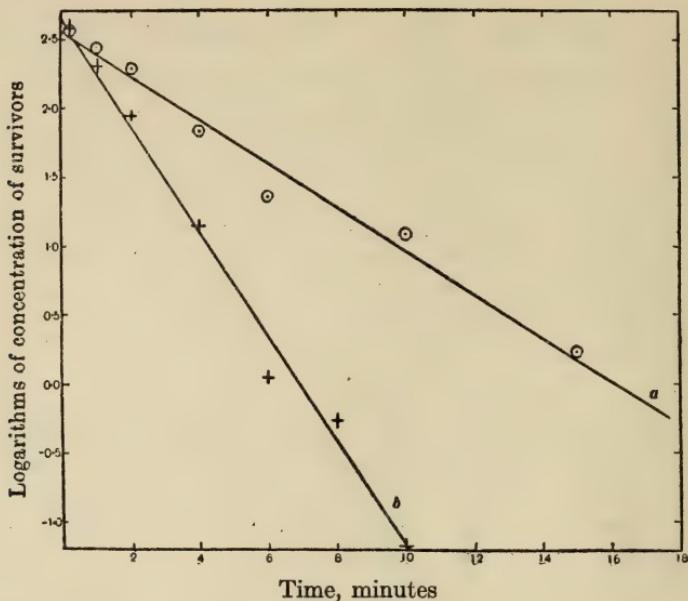


Fig. 4. Disinfection of *B. coli commune* with hot water (Table V).
 (a) EXP. I at 48.9°C. (b) EXP. II at 52.7°C.

DISINFECTANT ACTION OF SUNLIGHT AND DRYING

Drying. Paul & Prall (1907) while investigating the suitability of the "garnet" method for disinfection experiments with staphylococcus, allowed garnets, coated with a thin dry film of bacteria to remain at various temperatures and counted the surviving bacteria from time to time. It was found that while the number of living organisms remained constant for many weeks at the temperature of liquid air, the numbers slowly decreased at ordinary temperatures. Paul (1909) has analysed the above data and has shown that death by drying also proceeds in accordance with a logarithmic law. (See also Paul, Birstein & Reuss, 1910.)

Sunlight. There are only very scanty experimental data upon this subject, but in the work of Clark & Gage (1903) one experiment is given with *B. coli* which gives consistent results and on analysis shows the same relationship.

The results are set out in Table VI and fig. 5, page 179. The

concentration of survivors, determined from time to time by means of plate cultures; is seen to vary logarithmically with time, the value of the velocity constant, K remains fairly constant in value, and a straight line is obtained when logarithms of concentration of survivors are plotted against time, see Fig. 5.

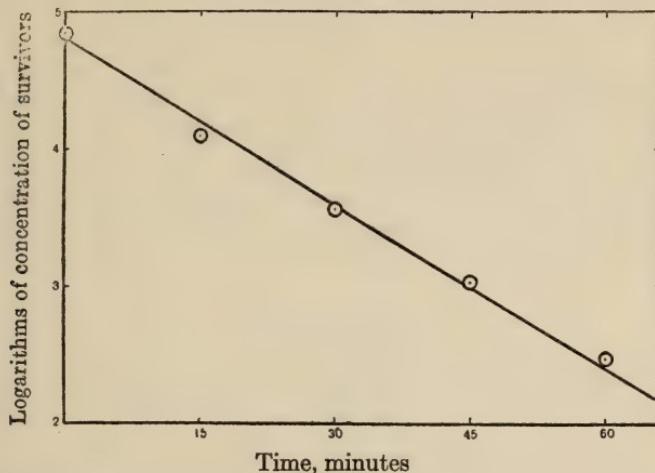


Fig. 5. Disinfection of *B. coli commune* by sunlight, results of Clark and Gage (1903), see Table VI.

TABLE VI.

*Disinfectant action of sunlight upon *B. coli commune*.*

(Clark and Gage, *Thirty-fourth Annual Report, State Board of Health, Massachusetts, 1903.*)

| Time, minutes $=t$ | Concentration of surviving bacteria, numbers per c.c. = N | $\log_{10}C$ | $K = \frac{1}{t_n - t_0} \log \frac{N_0}{N_n}$ |
|--------------------------|---|--------------|--|
| 0 = t_0 | 71400 = N_0 | 4.854 | — |
| 15 | 12365 | 4.092 | .051 |
| 30 | 3568 | 3.566 | .043 |
| 45 | 1065 | 3.027 | .041 |
| 60 | 295 | 2.470 | .040 |
| | | | Mean .044 |

It is not justifiable to draw a definite conclusion from such scanty data, but it is more than probable, judging from analogy, that the process of disinfection by sunlight will be found to fall in line with that experimentally established for other agents.

DISINFECTANT ACTION OF BLOOD-SERUM

In Table VII are given the results of a hitherto unpublished experiment with *B. colicommune* and normal rabbits' serum, at 30°C. After a latent period of about three and a half hours, disinfection proceeded slowly and in fair accordance with the logarithmic law (see values of the velocity constant in column 6).

TABLE VII

*Disinfection of B. Coli commune with normal rabbits' serum
at 30° C.*

EXP. 28. 11. 1912.

| Time, hours $=t$ | Amount of sample taken, drops | Numbers counted on plates, (gelatine) | Mean no. of surviving bacteria in 1 drop serum $=N$ | $\log_{10}N$ | K $= \frac{1}{tn-t_0} \log \frac{N_0}{N_n}$ |
|------------------------|---|--|---|--------------|--|
| 3.6 | 1 | 816 810 | 813 = N_0 | 2.910 | — |
| 4.1 | 1 | 532 538 | 535 | 2.728 | 0.36 |
| 4.5 | 1 | 396 392 | 394 | 2.595 | 0.35 |
| 5.0 | 1 | 263 276 | 269 | 2.430 | 0.34 |
| 5.7 | 1 | 117 123 | 120 | 2.079 | 0.40 |
| 6.4 | 1 | 57 42 | 48.5 | 1.686 | 0.44 |
| 7.0 | 1 | 29 33 | 31 | 1.491 | 0.42 |
| 8.2 | 1 | 30 20 | 25 | 1.398 | 0.33 |
| 9.1 | 1 | 16 18 | 17 | 1.230 | 0.30 |
| 10.2 | { 1 5 } | { 17 54 } | 11.8 | 1.072 | 0.28 |
| 11.4 | { 1 5 } | { 6 36 } | 5.3 | .724 | 0.28 |

SUGGESTED INTERPRETATION OF THE EXPERIMENTAL RESULTS

The foregoing examples may be taken as typical illustrations of the experimental data which is available. In the light of such evidence, disinfection must, in my opinion, be regarded as an orderly time-process presenting a close analogy with a chemical reaction, the bacteria and the disinfectant being regarded as the respective reagents.

The reaction proceeds according to some rule similar to the Mass Law so that if the disinfectant be present in large excess relative to the bacteria, disinfection proceeds in the same manner as a reaction of the first order, that is to say, as a unimolecular reaction, or, what amounts to the same thing, as a bimolecular reaction with one reagent in excess. The hydrolysis of cane sugar is an interesting parallel, viz.:—a union between water and sugar which nevertheless proceeds as a unimolecular reaction, for as ordinarily arranged the water is present in so great an excess that one may consider its concentration to remain constant and the reaction velocity to be determined only by the active mass of the second reagent, the sugar.

In the case of disinfection by hot water a complete analogy is presented with the heat coagulation of proteins, which in the ideal, uncomplicated case has been shown by Martin and the author (1910–1911) to be a “reaction of the first order.” The analogy is so close, being maintained as regards the accelerating effect of acids and alkalies, and the value of the temperature coefficient, that it is impossible to resist the conclusion that the death of bacteria by hot water is associated with the irreversible change caused by “heat coagulation” of the constituent proteins.

The reason, therefore, why disinfection by any of these means is not sudden, but gradual, and moreover proceeds in agreement with this well-defined logarithmic law, must be sought in the same direction as in the case of the decomposition of arsenious hydride, the inversion of sugar and the heat coagulation of proteins, all of which processes proceed as “uni-molecular” reactions. The explanation offered by the chemist in these instances is that at any one time, only a proportion of the molecules are in a condition to undergo the dissociation or chemical union as the case

may be. This *temporary* increase in susceptibility is believed to be occasioned by temporary differences in the internal energy of the molecules, which are distributed according to the law of chance. Accordingly the *proportion* of molecules, liable to attack at any moment, remains constant.

The process of disinfection may be explained on a similar hypothesis. Owing to internal fluctuating changes in the bacterial constituents, some individuals are liable to attack at one time, others at another, the total number of individuals vulnerable at any one moment being a constant proportion of the surviving population.

Such a view has not, however, received the support of some prominent bacteriologists who prefer a more vitalistic explanation. It has been common knowledge for many years that all individuals in a collection of apparently similar bacteria are not disinfected with equal ease, and this fact has been interpreted for example, by Bellei (1904) as an indication of differing degrees of resistance inherent in the bacteria, which can be accounted for by biological variation. More recently this view has received additional supporters among whom may be mentioned Eykman (1908), Hewlett (1909) and Reichel (1909, p. 152).

The following considerations form a powerful argument against their interpretation. Let us suppose that the progressive nature of the disinfection process may be attributed to *permanent* differences of resistance occurring among the various individual bacteria. If such were the case disinfection would certainly be gradual and not sudden, but the rate at any time would only be proportional to the concentration of survivors if the different resistances were allotted according to one definite arrangement, an arrangement which could only occur as a remote coincidence, and could hardly be universally present. For, suppose that the disinfection of 100,000 bacteria is in question, that the survivors vary logarithmically with time, as in the ideal case of disinfection, and that for the sake of argument the rate happens to be a reduction to 1/10th in each minute,

$$10,000 = 1/10 \text{ of } 100,000, \text{ survive after 1 minute,}$$

$$1,000 = 1/10 \text{ of } 10,000, \text{ will survive after 2 minutes, and}$$

$$100 = 1/10 \text{ of } 1000, \text{ will survive after 3 minutes,}$$

$$10 = 1/10 \text{ of } 100, \text{ will survive after 4 minutes, and so on}$$

If the cause of this is to be sought in the possession by the bacteria of different individual resistances to disinfection we should have to suppose that these resistances had the following distribution among the 100,000 bacteria, viz. that

90,000 take 1 minute to kill,
 9,000 take 2 minutes to kill,
 900 take 3 minutes to kill,
 90 take 4 minutes to kill, and so on.

Or, in the general case, if N bacteria die logarithmically, and if $1/x$ of N survive 1 minute, then

$1/x^2N$ will survive 2 minutes,
 $1/x^3N$ will survive 3 minutes, and so on,

and the resistance of the various individuals will be so distributed that there are present

$N - \frac{N}{x}$, or $N \frac{(x-1)}{x}$, which are killed in 1 minute,
 $N \left(\frac{x^2-1}{x^2} - \frac{x-1}{x} \right)$, or $N \frac{(x-1)}{x^2}$, which take 2 minutes to kill,
 $N \left(\frac{x^3-1}{x^3} - \frac{x^2-1}{x^2} - \frac{x-1}{x} \right)$, or $N \frac{(x-1)}{x^3}$, which take 3 minutes to kill,

and no other distribution will satisfy the necessary condition.

A further argument can be brought against a theory of variable permanent resistance, viz., that biological characteristic is as a rule distributed in a different manner. Those individuals possessing it in moderate amount are usually in the greatest number, while those possessing it in greater or less degree are in the minority. In the case of disinfection, those apparently possessing the least resistance are invariably in the greatest number.

Reichenbach (1911) admits the reasoning contained in the preceding paragraph, but has in an ingenious manner attempted to show that such a definite grading of resistances might nevertheless, under certain circumstances, be produced in a bacterial population owing to the peculiar¹ way in which this has its origin,

¹ Reichenbach's argument loses weight when it is remembered that the death of some higher organisms (Ehlamydomonas, Harvey, Annals of Botany, vol. XXIII, p. 181, 1909; seeds of barley, Darwin and Blackman, British Associa-

i. e. by continued subdivision of the existing organisms. This multiplication at first is general, but as time goes on is maintained by a decreasing proportion of the bacteria. Two assumptions are made, first, that the age of a bacterium and its resistance are bound up with one another and secondly, that the number remaining undivided in each successive generation increases with mathematical regularity.

Reichenbach feels forced to adopt some such explanation for the following reason. He considers it unlawful to extend an argument, based on chemical analogy, from a conceivable logarithmic destruction of constituent molecules of the bacterial cell, to explain the logarithmic death of the bacteria themselves. Taking the relative size of molecule and bacterium into account it is true that if the death of the latter occurred only after changes had taken place in a large number of constituent molecules, we might regard the various individual organisms as a series of similar vessels in which the same chemical reaction was running its course. If, in all, the conditions were exactly alike the reaction would in all cases arrive at the same stage at equal times. If then the death of a bacterium (or its inability to multiply further, which in all this work is taken as the criterion of death) is considered to be occasioned by a certain degree of internal destruction, a collection of similar individuals would all die after the same period of exposure to a disinfectant.

It must be admitted that the above argument is a real difficulty in the point of view I wish to advocate. In order to meet it one must assume that the constituent of the bacterium which is essentially concerned must be present in very small amount and that the number of its units are commensurate with the number of bacteria present, so that the bacteria themselves may be regarded as units in the process without gross inaccuracy.

In contradistinction to these theories of graded resistances, I would therefore explain the logarithmic nature of the distion, Dublin Meeting, 1909), under influence of poisons and hot water, also proceeds so that death-rate remains proportional to the concentration of survivors.

infection process as due to an essential *similarity* among the individual bacteria. For this view there is the following experimental support. It has been found that any circumstances which may be reasonably supposed to conduce to a more perfect uniformity among the individual bacteria, do not disturb the logarithmic precision of their disinfection, but make it the more perfect. On the other hand, where a departure from the law has been noticed, the cause has been traced to permanent dissimilarity among the units of the bacterial population.

The micro-organisms whose disinfection proceeds in most accurate agreement with the "unimolecular type" are the spores of *B. anthracis* whether suffering death by phenol mercuric chloride or hot water. In these cases the material had previously been heated to a high temperature ($80^{\circ}\text{C}.$) in order to kill any vegetative forms which might have been present. Incidentally any weakly spores also perished and the resulting collection of organisms possessed greater uniformity as regards resistance.

Disinfection of *B. paratyphosus* illustrates the converse argument.

In the case of 24 hours' cultures the rate of disinfection, whether by phenol or hot water, fell off more rapidly as disinfection proceeded than it should have done if proportional only to the concentration of surviving bacteria. This discrepancy was minimised and disinfection proceeded in nearer agreement with the ideal type, if experiments were made with material obtained by successively sub-culturing from broth to broth every 2-3 hours. (See fig. 6.)

It is probable from the researches of Lane-Claypon () and others that during the earlier hours of its life multiplication is very general among the population of a bacterial culture at $37^{\circ}\text{C}.$; later on the proportion of organisms remaining undivided becomes greater and greater as the concentration of bacteria approaches the limit which the medium can sustain. In a young culture therefore (sown also from a young culture to avoid admixture of veterans) the entire population will be of approximately the same age and generation. In a 24 hours' culture on the other hand there would obviously be less uniformity in this respect. It is very significant therefore that the former material

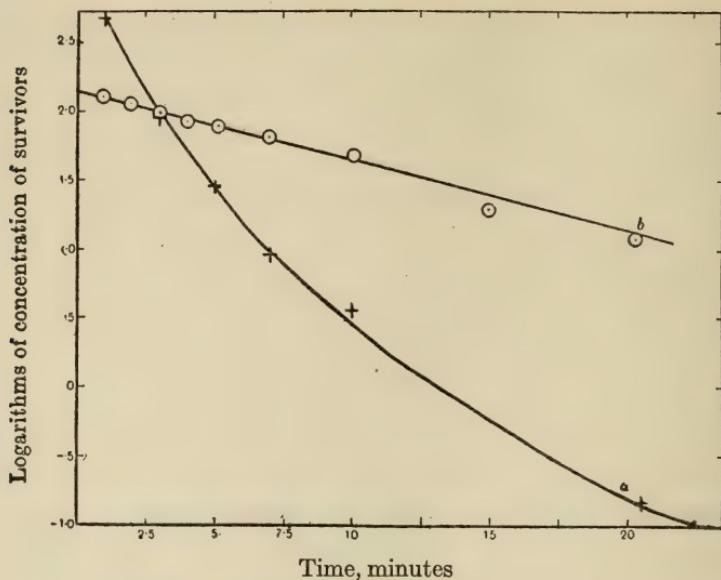


Fig. 6. (a) Disinfection of 24 hours' culture of *B. paratyphosus* with 0.6% phenol at 21°C. (H. C. 1908, Table VII.)

(b) Disinfection of 3 hours' culture (3rd generation of 3 hours' cultures) of *B. paratyphosus* with 0.6% phenol at 20°C. (H. C. 1908, Table XII.)

in disinfection should approximate more nearly to the ideal case.

The above interpretation of the facts of disinfection on the lines of chemical analogy has also received support from experimental data showing the influence upon reaction velocity of variation in

- (a) Concentration of Disinfectant.
- (b) Temperature.

(a) Concentration of Disinfectant

The ideal method of obtaining this information is by comparison of velocity-constants with varying concentration of disinfectant. This was, however, rejected owing to the extremely laborious nature of the necessary experiments, and an "end-point" method was substituted. The time was measured which was necessary for (almost) complete disinfection of a constant number of bacteria in various strengths of disinfectant at constant temperature; this time was taken to be inversely proportional to the mean reaction-velocity

of the process. In most cases about 30,000,000 bacteria were added to 5 c.c. disinfection mixture and samples ($=0.08$ c.c.) removed from time to time and tested for surviving bacteria by means of liquid sub-cultures. Disinfection-time was taken to be the period elapsing before a negative test-culture was obtained, strictly, the time taken for reduction of about 5 million organisms per c.c. to less than 60 per c.c. (i.e. when there is not one living bacterium in 0.8 c.c.).

A definite logarithmic relationship between velocity of disinfection and concentration of disinfectant was found to exist in all the cases investigated.

If the two variables were plotted one against the other the experimental points lay on regular curves. Fig. 7 below gives the results of disinfection by phenol of *B. paratyphosus* and *Staphylococcus pyogenes aureus* and may be taken as typical of a series of similar experiments.

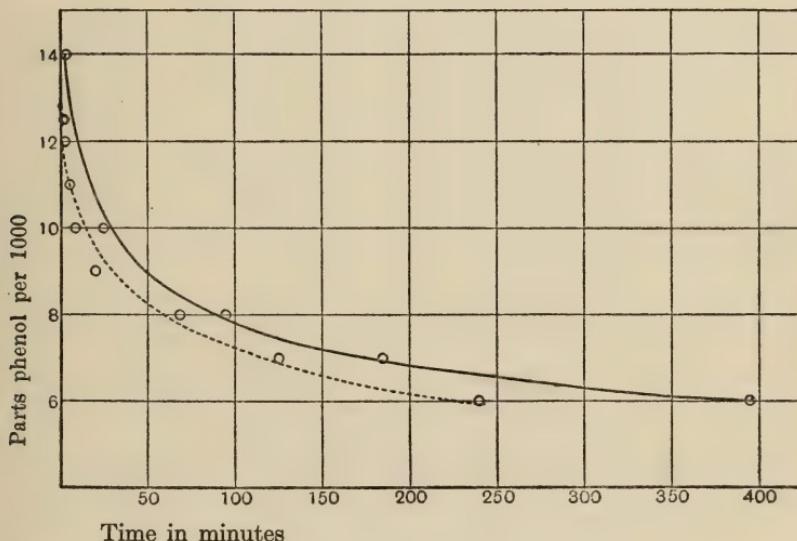


Fig. 7. Effect of varying the concentration of phenol upon the time taken for disinfection of (a) *B. paratyphosus*, dotted curve (H. C. 1908 Exp. 21. 6. 06, Table XVI): (b) *Staph. aureus*, continuous curve (Table XVII).

Watson (1908) has examined all the experimental data and showed that this logarithmic relationship may be expressed in the form

$$C^n t = \text{a constant},$$

or $\log C$ and $\log t = a$ constant, where $C =$ concentration of disinfectant and $t =$ time taken for disinfection.

TABLE VIII (H. C. 1908 Table XVI)

Phenol. *B. paratyphosus*. 20° C. 5 drops (.085 c.c.) of a 24 hours' broth culture (about 30,000,000 bacteria) added to 5 c.c. disinfectant solution.*

| | Parts phenol per 1000 $=C$ | Time taken for disinfection, i.e., reduction in number of about 30,000,000 individuals to less than 60 $=t$ | $5.5 \log C + \log t \dagger$ |
|---------------|----------------------------------|--|-------------------------------|
| EXP. 6. 6. 06 | 8 | 45 minutes | 6.62 |
| | 7.5 | 75 | 6.69 |
| | 7 | 105 | 6.67 |
| | 6.5 | 125 | 6.58 |
| | 6 | 225 | 6.64 |
| | 5.5 | 440 | 6.71 |
| | 5 | 11.5 hours | 6.68 |

* These and all subsequent values of the expression are calculated with Briggs' logarithms.

† See Watson (1908) Table I.

TABLE IX (H. C. 1908 Table XVII)

Phenol. *Staphylococcus pyogenes aureus*. 20° C.

| Phenol parts per 1000 $=C$ | Time taken for disinfection $=t$ | $5.5 \log C + \log t^*$ |
|----------------------------------|--|-------------------------|
| 14 | 4.5 minutes | 6.95 |
| 12.5 | 2.5 | 6.42 |
| 10 | 25 | 6.90 |
| 8 | 95 | 6.94 |
| 7 | 186 | 6.92 |
| 6 | 395 | 6.88 |
| 4 | 23.7 hours | 6.47 |

* See Watson (1908) Table II.

He has also pointed out that this is the relation which would hold for a chemical reaction where one molecule of one substance reacts with N molecules of a second, the latter being in great excess.

Tables VIII and IX show the value of the constant M in the two experiments with phenol set forth in fig. 7. It is noteworthy that the action of phenol upon the two organisms appears to be of the same character, the value of N being equal to 5.5 in either case. This indicates, according to Watson, that in the disinfection of *B. paratyphosus* or *Staphylococcus py. aur.* with phenol the molecules of phenol reacting those of the bacterial constituent are in the proportion of 5.5 to 1.¹

As regards metallic salts, the same law held good for disinfection by silver nitrate with a value of N , for *B. paratyphosus*, equal to 0.89. In the case of mercuric chloride, however, the above logarithmic relation between the concentration of disinfectant and the average velocity of disinfection is maintained only if the former is expressed in terms of the corresponding concentration of mercuric ions. Under these circumstances N has the value of 4.9 for anthrax spores (data of Krönig and Paul) and 3.8 for *B. paratyphosus*. This comprises the conclusion arrived at by Krönig and Paul that, in disinfection by metallic salts, the metallic ion is the real disinfecting agent. In the case of silver nitrate, electrolytic dissociation is so nearly complete in dilute solution, that the concentration of silver ions are in proportion to the concentration of the salt.

In these instances there is some evidence that disinfection is accompanied by a normal union of the metallic salt with the bacterial protein. A centrifuged deposit of bacteria previously treated with $HgCl_2$ although well washed, shows marked blackening on addition of SH_2 water.

Whether Watson's somewhat bold interpretation be correct or not, there seems to be no doubt that, as far as the available

¹ The matter would appear to be somewhat more complicated. The above may be true of the ultimate disinfection process. But it is probable from the researches of Reichel (1909) and Cooper (1912) that the first step in disinfection by phenol and other coal tar derivatives is a partition of the disinfectant between the water and the bacteria.

data go, the relation of average reaction-velocity, V_1 , of disinfection to concentration of disinfectant is expressed by the formula

$$C^n = KV. \text{ or}$$

$C^n t = K_2$ (where t , time of (almost) complete disinfection, is taken as proportional to the reciprocal of the average velocity of disinfection).

(b) Temperature

The results of a fairly comprehensive series of experiments show that the reaction velocity of disinfection is influenced by temperature in an orderly and consistent manner, in accordance with the law of Arrhenius. As regards the *magnitude* of the effect, disinfectants fall into two classes (1) those in which disinfection is accelerated by rise of temperature to a degree commensurate with that of most chemical reactions, *i.e.*, 2 to 4-fold for a rise of 10° C. and (2) those in which the effect of temperature is much greater.

Disinfection with mercuric chloride and silver nitrate fall into the first category.¹ Madsen and Nyman (1907) found the temperature coefficient for anthrax spores to be 2.5 for 10° C. rise in temperature over a range from 25° to 45° C. In Table X, which gives the results of two experiments with mercuric chloride and *B. paratyphosus* average disinfection-rate is seen to be accelerated about 3.5-fold for a rise in temperature of 10° C. between the temperatures of 0° and 42° C. The value of the constant $A = \frac{T_0 T_n}{T_0 - T_n} \log \frac{t_n}{t_0}$ (where t_n t_0 = times of disinfection (reciprocals of average velocity of disinfection) at the absolute temperatures T_n and T_0 , respectively) in the 4th column of Table X shows the degree of approximation to the law of Arrhenius.

¹ Disinfection by drying has also a low temperature coefficient viz.:—2-3 for 10° C. (Paul, 1909, Paul Birstein & Reuss, 1910).

TABLE X (H. C. 1908 Tables XXVII and XXVIII)
*Effect of temperature upon disinfection of *B. paratyphosus* with mercuric chloride*

| | Concen-tration of HgCl ₂ , parts per 1000 | Tem-perature degrees centi-grade | Time taken for disinfection† | Values of A $\left(= \frac{T_0 T_n}{T_0 - T_n} \log \frac{t_2}{t_1} \right)$, where initial absolute temperature $T_0 = 293$, and initial time $t_0 = 2.5$ | Relative increase in mean reaction-velocity for 10° C. rise in tempera-ture |
|---------------------|--|--|--|--|---|
| EXP. I. 9. iii. 07 | 1.0 | 42 29.7 20 12.6 7.9 0 | <0.5 min. <0.5 2.5 4.5 6 41.5 | — — — 2890 2590 4880 — Mean = 3420 | 3.9 |
| EXP. II. 6. iii. 07 | 0.1 | 41.6 30.7 19.8 13.9 6.8 0 | 0.75 2.5 11.5 36 50 101 | $T_0 = 314.6$ $t_0 = 0.75$ — 4580 5010 5480 4610 4390 — Mean = 4810 | 3.0 |

* These and all subsequent values of this expression are calculated with Briggs' logarithms.

† Strictly speaking, reduction of about 6,000,000 bacteria per c.c. to less than about 12 per c.c.

In the case of phenol and other coal-tar derivatives the effect of temperature is much more marked. Average velocity of disinfection was increased in the case of *B. paratyphosus* and phenol from 7-fold to 15-fold for a rise of 10° C., according to the strength of the disinfectant. The results of two experiments are given below in Table XI to serve as types. Some idea of the capacity

of this kind of work to yield accurate results, in other words of the possibility of obtaining constant conditions of experiment, may be gleaned from the fact that it was possible to fill up gaps in one experiment with results obtained on two other occasions.

TABLE XI (H. C. 1908 Tables XXXIII and XXXV)

*Effect of temperature upon disinfection of *B. paratyphosus* with phenol*

| | Concen- tration of phenol, parts per 1000 | Tem- perature degrees centi- grade | Time taken for disinfection | Value of A $(=\frac{T_0 T_n}{T_0 - T_n} \log \frac{t_n}{t_0})$, where initial abs. temp. T_0 = 308.7 and initial time $t_0 = 9$ | Relative increase in aver- age re- action— velocity for 10° C. rise in tempera- ture |
|-----------------|---|---|---|--|---|
| EXP. 27. ix. 06 | 6.0 | 44 35.7 30.5 28 25 21 16 6 | <1 minute 9 minutes 27.5 47.5 95 251 350 more than 10 hours | — — 8650 8660 8750 8890 7180 — Mean = 8430 | |
| EXP. I. x. 06 | | | | initial abs. temp. $T_0 = 303.5$ and initial time $t_0 = 1.5$ | 7.2 |
| EXP. 24. ix. 06 | 10.0 | 30.5 27.5 21.3 16.5 15.8 6 0 | 1.5 minute 3.5 minutes 9 27 23.5 226 17.5 hours | — * 8090 7870 7130 7530 7910 Mean = 7710 | |
| EXP. 26. ix. 06 | | | | | 7.5 |
| EXP. 25. x. 06 | | | | | |

* Figure obtained was not concordant.

† Strictly speaking, reduction of about 6,000,000 bacteria per c.c. to less than about 12 per c.c.

The temperature effect is of a still higher order of magnitude in disinfection by hot water. The velocity of disinfection is increased more than 100-fold per 10°C rise of temperature in case of *B. typhosus*, 29-fold per 10°C for *Staphylococcus pyogenes aureus*, 12-fold per 10°C for *B. coli*. The details of some experiments with *B. typhosus* are given in Table XII below, and in fig. 8 the logarithmic relation between disinfection-rate (reciprocal of times taken for disinfection) and the temperature of experiment is shown graphically.

TABLE XII (H. C. 1910. Table XXI)
Temperature coefficient of disinfection of B. typhosus with hot water (end-point method)

| | Temp. of exp., °C. | Time taken for disinfec- tion,* minutes = t | $\log_{10} t$ | \log_{10} (temper- ature co- efficient for 1°C.) | Tempera- ture coefficient per 1°C. | Tem- pera- ture coeffi- cient per 1°C. |
|---------------------|--------------------------|---|---------------|--|---|--|
| EXP. I, 10. 6. '09. | 59 | 1.26 | .100} | .250 | 1.78 | |
| | 54 | 22.5 | 1.352} | | | |
| | 49 | 196 | 2.292} | | | |
| EXP. II, 4. 6. '09 | 57 | 7.5 | .875} | .173 | 1.46 | |
| | 52.1 | 53 | 1.724} | | | |
| | | | | | | Mean 1.60 110 |

* Strictly speaking, reduction of about 5,000,000 per c.c. to less than about 12 per c.c.

A high temperature coefficient is characteristic of many reactions involving bodies of a protein nature (Famulener & Madsen, 1908; Madsen & Streng, 1909), including the coagulation of proteins by hot water, which has been found by Martin and the Author (1910) to be accelerated from 14 to 650 times. Hartridge (1912) finds the temperature coefficient for "heat coagulation" of alkaline methaemoglobin to be as great as 725 for 10°C rise in temperature in case of oxyhaemoglobin and egg-albumen respectively if the temperature is raised 10°C.

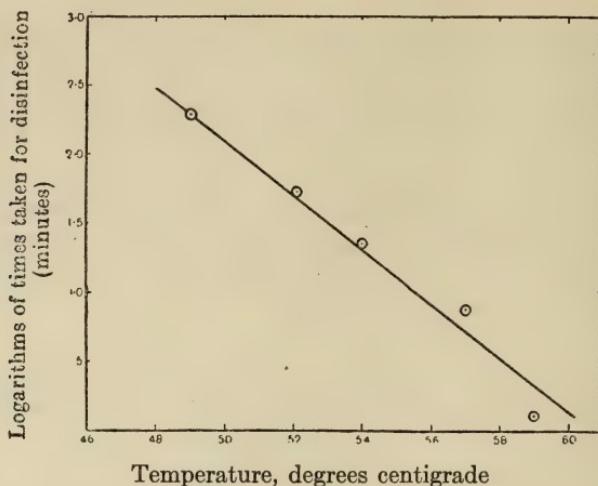


Fig. 8. Effect of different temperatures upon disinfection of *B. typhosus* by hot water (Table XII).

The logarithmic nature of the process in both coagulation of proteins and disinfection of bacteria by hot water, combined with the similar magnitude of the temperature coefficient indicates that the latter process is concerned with heat-coagulation of the constituent proteins. Additional confirmation is obtained from the exactly analogous effect of traces of acid and alkali in the two instances.

GENERAL CONCLUSIONS

The facts brought to light by the use of quantitative methods of study have shown disinfection in the ideal, uncomplicated, case to be an orderly time-process which is so arranged that the rate of disinfection at any moment is proportional to the concentration of surviving bacteria. This, in my opinion, can be most adequately explained by assuming an inherent similarity to exist between the various individuals so that their death will occur in accordance with the laws of chance, in other words a constant proportion of the surviving population will be killed in unit time. Yule (1910) has shown that if one condition is necessary for death, as a multitude of small causes, among a

number of similar individuals, death will occur logarithmically, if the result is governed by the law of probability.

In order to obtain a mental picture of the *way in which* these chance causes of death may operate, attention is naturally directed to the consideration of other processes which take place in a similar manner, viz.:—chemical reactions “of the first order” such as the decomposition of hydrogen arsenide, the inversion of sugar or the “heat coagulation” of proteins. The closest possible analogy has been demonstrated between the last instance and the destruction of bacteria by hot water.

In these cases an explanation has been sought in temporary changes in the energy of the molecules as a result of which all the molecules are not equally sensitive to attack at the same moment. Similarly, temporary changes in resistance are attributed to otherwise similar bacteria whereby at a given moment only a certain number will be vulnerable, that number being proportional to the total number of individuals surviving in unit volume.

Disinfection, whether by disinfectants, heat or other agencies, exhibits the closest analogies with a chemical reaction, the velocity of which is controlled by external conditions, such as temperature or the concentration of bacteria and disinfectant.

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STUDIES OF FISH LIFE AND WATER POLLUTION

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The effect of sewage, trade wastes and the effluents from sewage filters, upon fish life has received little investigation in this country, although it is known, of course, in a general way that owing to increasing pollution, fish have disappeared from many streams in which they were formerly abundant.¹ The effect of sewage pollution upon shellfish and the areas from which shellfish are taken, has been investigated during the past ten or fifteen years chiefly because shellfish are likely to be the bearers of infectious diseases.

From a practical point of view the question of fish life in streams in a settled community is one of the value of such life in a certain stream or lake compared with the cost of maintaining such freedom from pollution or such restrictions in the use of streams as will allow the continuance of this life. It goes without saying that looked at in this way, the cost of preserving a stream in a condition that allowed such life might be exceedingly large as compared with the value of the fish saved. This would be especially true in manufacturing districts, as in such places the streams are chiefly valuable for power and the carrying away of the waste products of the districts more or less purified. Treating these wastes sufficiently to prevent the stream from becoming a nuisance, moreover, may not keep it sufficiently pure to encourage the life of fish within it. Many streams are fated to become sources of power and the carriers of wastes, and find their chief value when so used. Practically all that can be expected in many instances is that the sewage or wastes entering such streams, shall at all times of the year be so purified before entrance or so diluted by the flow of water that the stream will not be a nuisance to the community through which it flows but rather a source of enjoyment to such community.

¹ When the work described in the following pages was begun rather more than a year ago, the writers were not aware of certain investigations that had been made abroad and that have since been brought to their attention.

From a scientific standpoint there are a number of questions to be considered in this study of pollution and fish life, the most important being as follows: (1) the amount of pollution that a stream may receive without decreasing the dissolved oxygen of the water to such a degree that fish can no longer live in the water; (2) the effect of the various constituents of sewage and trade wastes upon fish and the effect of these various constituents upon fish even when a plentiful supply of dissolved oxygen remains in the waters after receiving these wastes; (3) the amount of oxygen consumed by the fish themselves; and (4) the rate of absorption of oxygen by polluted waters.

There are other questions involved that will be mentioned in the following pages. At the Lawrence Experiment Station of the Massachusetts State Board of Health a series of investigations in regard to these questions has been carried on during the past year. The experiments have been made largely in five-gallon glass aquaria and the commonest fish of the region,—shiners, suckers, chub and carp have been used. Most of the carp and shiners have weighed from one to two ounces each, while the suckers have weighed from one-quarter to one-half pound.

EFFECT OF SEWAGE

In the first experiments, the fish were immersed in undiluted Lawrence sewage, well aerated, and containing at the time of immersion from 50 to 100 per cent. of saturation of dissolved oxygen. Notwithstanding the presence of this dissolved oxygen, all the fish in these experiments apparently became crazed when immersed and died almost immediately, that is, within a few minutes after immersion.

EFFECT OF EFFLUENTS FROM SEWAGE FILTERS

Following this, experiments were made with the effluents from sand, contact and trickling filters and with mixtures of sewage and water, contact filter effluents and water and trickling filter effluents and water. In all these series of experiments a supply of dissolved oxygen was maintained when necessary by blowing air through the liquid used. The results were as follows:—

(a) It was found that when water and sewage were mixed in equal portions and this mixture kept aerated, fish life could exist almost indefinitely, but with a larger proportion of sewage of the strength used, the fish died within a few minutes or at most in an hour or two after their immersion. Even in the equal mixtures of sewage and water, a number of fish died quickly and only the stronger individuals survived, but such as did survive were kept in this mixture alive and well for fourteen days and apparently could have continued to live for an indefinite period. The sewage used was freed from matters in suspension before being mixed with the water.

(b) It was found that effluents from contact and trickling filters in successful operation, when kept aerated supported fish life for fourteen days without any apparent discomfort to the fish immersed in these effluents.

The following table presents the analyses of the mixture of sewage and water, and of the effluents from contact and trickling filters used in these experiments.

(Parts per 100,000)

| | Contact Filter Effluent. | | Trickling Filter Effluent. | | Equal Mixture of Water and Sewage. | |
|--|-----------------------------|-------------------|-------------------------------|-------------------|--|-------------------|
| | At Start. | After 14 Days. | At Start. | After 14 Days. | At Start. | After 14 Days. |
| Free Ammonia.... | 1.5500 | 2.8000 | 1.8000 | 2.8800 | 1.9000 | 2.8000 |
| Albuminoid Ammo- nia, Total..... | 0.2700 | 0.2880 | 0.2800 | 0.3480 | 0.2100 | 0.2280 |
| In Solution..... | 0.1540 | 0.1840 | 0.1800 | 0.1220 | 0.2100 | 0.1480 |
| Chlorine..... | 11.30 | 12.40 | 10.70 | 12.10 | 7.30 | 7.00 |
| Nitrogen as Nitrates..... | 0.03 | 0.04 | 2.01 | 2.12 | 0.02 | 0.02 |
| Nitrites..... | 0.0000 | 0.0000 | 0.0100 | 0.0600 | 0.0024 | 0.0180 |
| Oxygen Consumed. | 1.78 | 1.80 | 1.82 | 2.22 | 1.24 | 1.46 |
| Solids in Suspension Total..... | | | | | 0.0 | 2.3 |
| Volatile..... | | | | | 0.0 | 2.2 |

EFFECT OF SEWAGE AND EFFLUENTS WHEN NON-AERATED

Experiments were next made to determine the volume of water (tap water) necessary to mix with sewage and the effluents from trickling filters in order that fish life might be sustained under what might be called stagnant conditions, that is, sustained without the introduction of dissolved oxygen by aeration as in the previous experiments. After several trials it was found that but 10 per cent. of sewage could be mixed with 90 per cent. of water and the fish survive in good condition for fourteen days. Increasing the proportion of sewage above this percentage invariably caused the exhaustion of the oxygen and the death of the fish within a few hours. It was found that only 25 per cent. of water was needed in 75 per cent. of the best trickling filter effluents in order that fish might live under these stagnant conditions for fourteen days, this mixture always containing enough oxygen to support life, and the effluent present having apparently no harmful effect upon the fish. With the contact filter effluents equal mixtures were necessary, that is, 50 per cent. of the effluent to 50 per cent. of tap water.

DISSOLVED OXYGEN

At the beginning of the last experiments described, that is, at the time of the immersion of the fish, the dissolved oxygen in the mixtures was 0.50 part per 100,000. During the experiment it became reduced in the water and effluent mixture to as low a point as 0.11 part per 100,000, and in the mixture of sewage and water, to 0.14 part per 100,000 but without any apparent discomfort to the fish in these mixtures.

The greatest consumption of oxygen by the organic matter present in such mixtures occurs in the first few hours, and it was found that if the initial supply of oxygen was great enough to last through this early period, the oxygen would then be increased by absorption from the air.

In a third experiment of this nature, where a mixture of equal portions of tap water and trickling filter effluent was made, the dissolved oxygen at the start was 0.80 part per 100,000 and was

not reduced below 0.40 part per 100,000 during the fourteen days of the experiment.

The table following shows the analyses of these mixtures at the beginning and at the end of these experiments.

(Parts per 100,000)

| | Water and 75 Per Cent. Trick- ling Filter Efflu- ent. | | Water and 10 Per Cent. Sew- age. | | Water and 50 Per Cent. Trick- ling Filter Efflu- ent. | |
|------------------------------|--|-------------------|--|-------------------|--|-------------------|
| | At Start. | After 14 Days. | At Start. | After 14 Days. | At Start. | After 14 Days. |
| Free Ammonia.... | 1.2000 | 1.8800 | 0.5500 | 0.6600 | 1.3000 | 1.2600 |
| Albuminoid Am- monia..... | | | | | | |
| Total..... | 0.0960 | 0.1720 | 0.0440 | 0.0620 | 0.1260 | 0.1000 |
| In Solution..... | 0.0960 | 0.0820 | | 0.0300 | 0.0840 | 0.0720 |
| Chlorine..... | 7.20 | 7.10 | 1.60 | 2.00 | 6.50 | 6.50 |
| Nitrogen as | | | | | | |
| Nitrates..... | 2.09 | 1.81 | 0.06 | 0.06 | 0.67 | 0.50 |
| Nitrites..... | 0.0064 | 0.0380 | 0.0000 | 0.0036 | 0.0015 | 0.0340 |
| Oxygen Consumed. | 0.90 | 1.00 | 0.63 | 0.67 | 1.00 | 1.04 |
| Solids in Suspension, | | | | | | |
| Total..... | 0.0 | 1.9 | | | | |
| Volatile..... | 0.0 | 1.6 | | | | |

In further investigations in regard to the amount of dissolved oxygen that would sustain fish life, the following three experiments were made:—Sewage of the strength shown in the table following was so mixed with city water that three dilutions containing 5, 10 and 15 per cent., respectively, of sewage were obtained. In these dilutions the dissolved oxygen was at first 0.88, 1.00 and 0.85 parts per 100,000. In each dilution fish were immersed and in each of the three dilutions they lived for one week without discomfort, that is, until the end of the experiment. The minimum amount of dissolved oxygen found during this period in each of these dilutions was 0.47, 0.28 and 0.15 part per 100,000, respectively.

SEWAGE

(Parts per 100,000)

| Ammonia. | | Albumi-noid. In Solution. | Kjeldahl Nitrogen. | | Chlorine. | Oxygen Consumed. |
|----------|--------|---------------------------------|--------------------|-----------------|-----------|---------------------|
| Free. | Total. | | Total. | In Solution. | | |
| 5.80 | 0.86 | 0.35 | 1.38 | 0.79 | 12.40 | 4.40 |

EFFECT OF SAND FILTER EFFLUENTS

In six experiments in which fish were immersed in well-purified, highly nitrified effluents from sand filters receiving sewage, the three fish immersed in each experiment, died in from three hours to three days after immersion. All of these effluents but one were clear but slightly acid, this acidity being due to insufficient base to combine with the nitric acid present. One effluent was alkaline but contained considerable matter in suspension, this matter being largely silica and alumina. When this suspended matter was removed the fish lived in this effluent without any apparent discomfort for fourteen days or during the length of the experiment. Other acid effluents from sand filters when neutralized and filtered to remove precipitated CaCO_3 and MgCO_3 , etc., supported fish life. The alkaline suspended matters at times separating from such effluents and from sewage, gathering at the outlet of the fish's gills and at the joints in their scales, gave the appearance of a fungus growth upon the fish.

The following table presents the results of analyses of the effluents used in these experiments.

EFFLUENTS FROM SAND FILTERS RECEIVING SEWAGE

(Parts per 100,000)

| Ex- peri- ment No. | Ammonia. | | Chlo- rine. | Nitrogen as | | Oxygen Con- sumed. | Alka- linity. |
|-----------------------------|----------|---------------------------|----------------|-------------|-----------|--------------------------|------------------|
| | Free. | Total Albumi- noid. | | Nitrates. | Nitrites. | | |
| 1 ... | 0.4800 | .0540 | 9.00 | 5.21 | .0024 | .23 | -0.9 |
| 2 ... | 0.9600 | .0960 | 7.30 | 1.64 | .0032 | .51 | -0.3 |
| 3 ... | 0.9600 | .0960 | 9.40 | 2.17 | .0120 | .54 | 1.0 |
| 4 ... | 0.0628 | .0194 | 9.00 | 4.62 | .0002 | .17 | -0.2 |
| 5 ... | 1.0400 | .0460 | 7.10 | 6.13 | .0012 | .45 | -1.5 |
| 6 ... | 0.2505 | .0290 | 7.00 | 1.64 | .0380 | .29 | -0.2 |

EFFECT OF NITRATES, IRON, POTASSIUM, CARBONATE, ETC.

It would seem without doubt that the alkaline suspended matter and the acidity of the effluents in the experiments just described, were responsible for the death of the fish immersed within them.

Fish immersed in water containing 5 parts of nitrogen as potassium nitrate, lived without any apparent discomfort, and in water in which organic matter, etc., had been coagulated by the use of 1.5 grains of alum, they lived two weeks without discomfort.

In water treated with ferric sulphate they became covered with a fungus-like growth and died in a few days. The iron in solution may have been the cause, as apparently fish are extremely sensitive to iron salts as will be shown later.

Free nitric acid in tap water in amounts equal to 0.7 part per 100,000 CaCO_3 was without effect.

Very small amounts of hydrochloric acid not greater than -0.5 part per 100,000, caused the death of fish in a few hours.

When the experiments with nitric acid were made, it was found that the small fish used not only neutralized the acid but made the water alkaline. The water was acidified five times and

each time was rendered alkaline by the fish present. In twelve days the fish experimented with had neutralized acid equal to 2.7 parts per 100,000 CaCO_3 in about 1500 c.c. of water, leaving a residual alkalinity of -1.0 part per 100,000.

"Free ammonia" in sewage is supposed to consist in part of carbonate, and it was found that from 5.5 to 7.0 parts of ammonia as carbonate in well aerated tap water, was fatal to shiners and carp in from a few minutes to a few hours. Ammonia in the form of chloride up to 18.0 parts per 100,000 had no ill effect on the fish. When used in the form of ammonium hydrate, the ammonia was much more deadly, 2.0 parts per 100,000 killing shiners, carp and large suckers in fifteen minutes. The fatal amount was probably slightly over 1.0 part per 100,000 as the fish experimented with were unaffected in water containing 0.94 part per 100,000 but died in water containing 1.3 parts per 100,000.

It should be noted in passing that the ammonium hydrate is soon changed in water to the less injurious carbonate by the free carbonic acid present and by carbonic acid given off by the life of the fish.

The effect of caustic and carbonate alkali was next tried. Pollution of this nature comes from a number of industrial processes and at times may be serious before sufficient dilution by the water in a stream takes place to render it harmless. It was found that from 25.0 to 30.0 parts per 100,000 NaCO_3 per 100,000 killed fish within a few hours. Seven parts of NaOH killed several in two hours and 9.6 parts per 100,000 killed two in ten minutes. In water containing 5.6 parts per 100,000, fish lived twenty-four hours.

It was noticed in this work that fish immersed in sodium carbonate solutions, rendered these solutions less poisonous to fish subsequently immersed in them, this being due probably to the change from carbonate to bicarbonate. As a proof of this, it was found that bicarbonate of soda was the least injurious form of alkali experimented with, fish living easily in water containing 120.0 parts per 100,000.

The effect of iron salts was next investigated, these salts being dissolved in distilled water to prevent precipitation such as would occur in tap water on account of the alkalinity of this tap water.

Copperas equivalent to 0.128 part per 100,000 of iron killed fish in from four to twenty-four hours, one fish living without trouble in water containing 0.100 part per 100,000. In such dilute solutions, however, the iron gradually precipitates even when dissolved in distilled water.

In solutions of ferric sulphate fish died in from one-half hour to three hours when 0.1080 part iron per 100,000 was present and in from twelve to twenty-four hours when as little as 0.0100 part per 100,000 was present.

CONSUMPTION OF OXYGEN BY FISH LIFE

The large amount of dissolved oxygen breathed by fish is little realized. In studying this point, the following experiments were made:—Thirteen small fish weighing altogether 200 grams were placed in a Saltmouth gallon bottle filled with water, and the dissolved oxygen determined at the beginning and at the end of the experiment.

In a second experiment four fish weighing 340 grams were used. In all, nine experiments of this kind were made. Averaging these experiments it was found, speaking generally, that all the oxygen held in solution in a gallon of water at 60°F.,—practically one part per 100,000,—would be consumed or breathed in one hour by a weight of fish equal to one pound. This would mean that 1,000 pounds of fish life would in about fifteen days exhaust the dissolved oxygen in a layer of water one foot deep and an acre in area, saturated at 60° F., allowing, of course, that dissolved oxygen was not added by absorption from the air. The oxygen consumed in this way remains in the water as CO₂ and hence the amount of CO₂ in surface waters sustaining fish life must be influenced to a considerable extent by the fish present.

SOLUTION AND DIFFUSION OF OXYGEN IN WATER

There are few good data in regard to the rate of solution and diffusion of oxygen in water. E. A. Letts in the Journal of the Royal Sanitary Institute, Vol. XXXIII, No. 1, states that Dr. Adeny found that ten days were required to saturate with oxygen

a sheet of water with a temperature of 15°C., 6 feet in depth, and deprived of all atmospheric gases.

The following experiments made by us give some idea of the rate of aeration of a quiet, shallow sheet of water. In the first, a small fish, weighing 25 grams, was immersed in an aquarium holding 7 inches in depth of tap water. Experiments had shown that a fish of this size in this volume of water would reduce the dissolved oxygen primarily present about 0.26 part per 100,000 per day.

The following table presents the amount of dissolved oxygen found in the water in the aquarium on different days during a period of thirty-four days, together with a column showing the amount of oxygen consumed by the fish during that period. From this table it will be seen that oxygen was absorbed by the water at about the same rate that it was consumed by the fish.

| Days. | Dissolved Oxygen. | |
|---------|-------------------|--------------------------------------|
| | In Aquarium. | Used by Fish. (Parts per 100,000) |
| 1..... | .37 | 0.26 |
| 2..... | .40 | 0.52 |
| 3..... | .45 | 0.78 |
| 5..... | .22 | 1.04 |
| 14..... | .49 | 3.18 |
| 22..... | .40 | 5.48 |
| 29..... | .50 | 7.08 |
| 34..... | .31 | 8.58 |

In a second experiment the dissolved oxygen in an aquarium of tap water was reduced to 0.11 part per 100,000 by the fish in this aquarium. The fish were then removed and the aquarium allowed to stand in the laboratory open to the air, and determinations of dissolved oxygen made from time to time. The results of these determinations are shown in the following table and it will be noticed that practically seven days were required for this water to again become saturated with oxygen.

| Days. | Tempera-ture Deg. F. | Dissolved Oxygen. | |
|---------|-------------------------|-----------------------|------------------------------|
| | | Parts per 100,000. | Per Cent. of Satura-tion. |
| 2..... | 68 | 0.38 | 41.3 |
| 3..... | 65 | 0.72 | 74.7 |
| 4..... | 64 | 0.76 | 79.2 |
| 5..... | 66 | 0.80 | 85.0 |
| 6..... | 67 | 0.88 | 94.5 |
| 7..... | 70 | 0.94 | 104.0 |
| 10..... | 65 | 1.00 | 105.0 |

During the last part of this experiment, "green growths" (Scenedesmus and Protococcus) made their appearance in this water.

LIBERATION OF OXYGEN BY "GREEN GROWTHS"

It is well known that organisms containing chlorophyll give off free oxygen when growing in the light. Water in which organisms are plentiful is frequently found to be supersaturated with dissolved oxygen as the organisms take the C from the CO₂ dissolved in the water, and liberate part of the oxygen. When the dissolved CO₂ is all absorbed the bicarbonates are attacked and CO₂ abstracted, leaving carbonates. This happened several times in experiments here. On testing for CO₂ with phenolphthalein, a pink color showed the presence of carbonates, while in the tap water used in the various experiments, the alkalinity was due to bicarbonates. In these experiments the "green growths" were largely Protococcus, Scenedesmus and smaller numbers of Monas. In one experiment an aquarium was filled with tap water and seeded with "green growth." The dissolved oxygen and CO₂ at the start were 0.18 and 1.0 parts per 100,000, respectively. At the end of seven days, they were 1.14 and 0.0 parts per 100,000, respectively.

In another experiment a small fish was put into a tightly-stoppered gallon bottle full of water containing these "green growths." If oxygen had not been liberated by the organisms during this experiment, the oxygen primarily present would have been consumed by the fish in thirty-eight hours. However, it lived eight days and at its death at the end of this period, dissolved oxygen was present in the water in greater volume than at the beginning of the experiment. The growth of organisms increased greatly during this period and either the presence of these organisms or some body formed during their growth or decay, was injurious to the fish.

In a similar experiment made during cloudy weather when the oxygen-liberating power of the organisms was lowered, the fish present consumed the dissolved oxygen in four days.

In further experiments, not yet completed, upon the effect of such "green growths" on sewage, bottles of sewage were seeded with organisms, then aerated for twenty-four hours and afterwards allowed to stand twenty-four hours without artificial aeration. The average of sixteen dissolved oxygen determinations then made showed 0.62 part per 100,000 of dissolved oxygen present in these sewages at the end of the period of aeration and 1.01 parts per 100,000 after the sewage had stood unaerated during an additional period of twenty-four hours; in other words, the "green growth" supplied not only all the dissolved oxygen consumed by the sewage during the period of standing but, furthermore, increased the volume present 0.39 part per 100,000.

It is probable that the chlorophyll-bearing organisms take a greater part in overcoming sewage pollution in surface waters than is at present generally realized.

DETERMINATION OF NITRATES IN SEA WATER

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The importance which attaches to a reliable method for the quantitative estimation of nitrates in sea and land waters and mixtures of the two depends chiefly upon the light which this test, in combination with determinations of albuminoid and free ammonia and nitrites, can throw upon problems of the pollution by sewage of tidal harbors and the sea.

Given the amount of nitrogen present in each of the four stages of change from albuminoid ammonia to nitrates, a definite idea may be formed not only of the whole burden of contamination, but of the recentness of the pollution or, if this be known, the rate at which the sewage is being assimilated. If the nitrogen in any of the four stages is unknown, the information obtainable from the remainder must be regarded as fragmentary.

In the investigations made by the Metropolitan Sewerage Commission, which have included several thousand analyses of the waters of New York harbor, the usual methods of analysis suitable for the water of inland rivers and lakes were found to give unreliable results as regards nitrates. The sulphanilic acid method failed. It was not known that any method could be depended upon. Many analysts were of opinion that nitrates did not exist in sea water, and papers were read at the last International Congress on Applied Chemistry which seemed to prove that this was true. (See Purvis and Coleman.)

It was desirable to know whether nitrates were present and, if so, in what amount. After some preliminary investigation, it was decided to test the two most promising methods for the electrolytic reduction of nitrates to the form of ammonia and the subsequent estimation of the ammonia in the usual way. The reduction procedures which were compared were the copper zinc method, as described by McGowan (See Part V Vol. IV,

Fourth Report Royal Commission on Sewage Disposal of Great Britain) and the aluminum foil method, as recommended by the Committee on Standard Methods of Water Analysis of the American Public Health Association. Parallel tests were made with these, using sea water, harbor water and land water. Definite weights of sodium nitrate were added and the increases noted by analysis.

The results of the research show that nitrates were present in all the samples and that nitrates in sea water and mixtures of sea water and land water can be reliably determined by either of the reduction methods tested. The data obtained in these experiments follow:

TABLE NO. 1

Amount of Nitrogen Found, as Nitrate in Land, Harbor and Sea Water, by Reduction—(a) with Aluminium Foil, and (b) with Copper Zinc Couple

| Source of Sample | Parts per 1,000,000 | |
|--------------------|------------------------------------|--------------------------------------|
| | Series A Aluminium Reduction | Series B Copper Zinc Reduction |
| Land Water | 0.004,0 | 0.366,0 |
| " " | 0.291,0 | 0.300,0 |
| Harbor Water | 0.425,0 | 0.445,0 |
| " " | 0.520,0 | 0.560,0 |
| Sea Water..... | 0.240,0 | 0.260,0 |
| " " | 0.160,0 | 0.160,0 |
| " " | 0.100,0 | 0.180,0 |

TABLE NO. 2

Amount of Nitrogen Found, as Nitrate in Land and Sea Water Charged with Known Quantities of KNO_3 , by Reduction—(a) with Aluminium Foil, and (b) with Copper Zinc Couple

| Source of Sample | Present Theoreti- cally | Parts per 1,000,000 | |
|------------------|-------------------------------|------------------------------------|--------------------------------------|
| | | Series A Aluminium Reduction | Series B Copper Zinc Reduction |
| Land Water..... | 0.005,2 | 0.005,0 | 0.005,0 |
| Sea Water..... | 0.138,0 | 0.127,0 | 0.131,0 |
| " " | 0.011,0 | 0.010,0 | 0.010,0 |
| " " | 0.005,5 | 0.005,0 | 0.004,5 |
| " " | 0.005,5 | 0.005,1 | 0.006,0 |
| " " | 0.010,0 | 0.010,0 | 0.007,5 |
| " " | 0.016,5 | 0.015,0 | 0.016,5 |
| " " | 0.035,0 | 0.033,0 | 0.035,0 |

WHAT HYPOCHLORITE STERILIZATION OF WATER SUPPLIES HAS ACCOMPLISHED IN SEVERAL CITIES

C. A. JENNINGS

Chicago, Ill.

Sterilizing municipal water supplies with hypochlorite of lime (chloride of lime) is of comparatively recent origin. It dates back to the Summer of 1908 when Mr. Geo. A. Johnson of New York recommended its use at the "Bubbly Creek" filter plant at the Union Stock Yards in Chicago. The fact that it was successful there and that its application was so simple and yet so effective in destroying the harmless as well as the pathogenic bacteria found in water supplies, caused it to be quickly adopted as both an emergency and permanent treatment by many cities. Today there are probably 300 or 350 cities using this process. It has the advantage over ozone and ultraviolet ray sterilization of being more economical of installation as well as operation and yet it is just as effective as either. The cost of chemicals for the hypochlorite treatment will range from 10 to about 40 cents per million gallons treated, the operating and depreciation charges being very small. The cost for attendance will vary within wide limits, depending to a large extent on the character and number of attendants employed, the amount of water treated daily and whether it is the only treatment used or whether it is used as an adjunct to some other process, such as filtration, etc. At one plant with which the writer is thoroughly familiar, 15,000,000 gal. per day are treated with hypochlorite at a cost of 96 cents per million gallons for chemical, labor, power and supervision. The superintendent is also chemist for the water department, analyzing coal, oil, gas, etc. This plant, built with concrete tanks, mechanically driven agitators, recording devices and all the latest improvements, cost about \$3,500 complete. At another plant, treating 30,000,000 gal. per day, the

cost of operation including chemical, labor and power, is only 27.6 cents per million gal. The city chemist whose salary is not included in this figure, has supervision over the operation of the plant.

New York City is now building a sterilization plant to treat the entire water supply from both the old and the new Croton aqueducts, supplying the boroughs of Manhattan and the Bronx, the flow of which may reach a maximum of 380,000,000 gal. per day. This plant will be in operation by the Fall of 1912. Other large cities now using this treatment to sterilize their water supplies are:—Pittsburg and Philadelphia, Pa., Minneapolis Minn., Cleveland and Cincinnati, Ohio; Omaha, Nebr., Indianapolis and Terre Haute, Ind., Kansas City, Mo., Little Falls, and Jersey City, N. J., Des Moines, Council Bluffs and Davenport, Iowa; Nashville, Tenn., Denver, Colo., Brooklyn, N. Y., and Baltimore, Md. Among the cities in other countries using the hypochlorite treatment might be mentioned:—Toronto, Montreal and Ottawa, Canada; Cambridge, Worthing and Poplar, England; Middlekerke, Belgium; Paris and Nice, France; Vera Cruz, Mexico, and Havana, Cuba.

The hypochlorite treatment can be used alone as at Cleveland and Erie, with impounding reservoirs at Jersey City and Baltimore, with sedimentation basins at Nashville and Omaha, with infiltration systems at Des Moines, with slow sand filters at Pittsburg and Indianapolis, with pressure filters at Davenport and Terre Haute, with rapid sand filters at Cincinnati and Cedar Rapids, with mountain streams at North Yakima and Grants Pass and with well water supplies as at Corning. The action of the chemical is purely germicidal, oxidizing the organic matter and bacteria. It does not reduce the turbidity and the color only to a slight extent.

So widespread has been the use of hypochlorite and so effective in stopping Typhoid Fever epidemics when water-borne, that the boards of health of at least four states have constructed portable treatment plants that can be sent out by express on short notice and set up ready for operation within a few hours after delivery. These states are Indiana, Michigan, Minnesota, and Kansas. Whereas it requires months to install a filter

plant, a hypochlorite plant can be put into operation in a few days and even hours, if urgent. It is a valuable adjunct to a filtration system, which at best removes only 97% or 98% of the bacteria without any particular selective action. The hypochlorite treatment used in conjunction with filtration, will at a very small additional expense, increase the bacterial removal to from 99.0% to 99.9%.

The hypochlorite of lime treatment during the past four years has saved hundreds of lives. At Erie, Millvale and Coatesville, Pa., Ottawa and Strathcona, Canada; Des Moines and Council Bluffs, Iowa; Minneapolis, Minn., North Yakima, Wash., Evans-ton and Waukegan, Ill., Typhoid Fever epidemics were successfully and quickly terminated by the use of this treatment.

In considering Typhoid Fever statistics before and after the introduction of the hypochlorite treatment, it is often very difficult to make a fair comparison for the reason that there is a woeful laxity in reporting these statistics in many cities. This is usually conscientiously looked after following an epidemic but seldom previous to one. However, the writer has gathered sufficient reliable bacteriological data as well as Typhoid Fever statistics to show the effect that sterilization has had on the bacterial content of the water and on the reduction in the number of deaths and cases from Typhoid Fever.

Terre Haute, Ind., has a pressure filter plant. The average bacterial data for Feb., Mch., and April 1912 was:—Raw water 3,870 per cc., with *B. Coli* present in 68% of the samples tested, while the filtered and sterilized water showed only 34 per cc., with *B. Coli* absent in every sample tested. Samples were collected daily.

Cedar Rapids, Iowa, began using hypochlorite in March 1912 as an adjunct to their rapid sand filters and the results have been spectacular. During the period from March 29 to May 15, 1912, the raw water averaged 40,200 bacteria per cc., filtration alone showed a reduction in bacteria to 1,700 per cc., or 95.8%, while the hypochlorite treated water count was only 44 per cc., or a total reduction of 99.9%. *B. Coli* was present in 63% of the raw water samples examined, in 36% of the filtered water

samples but not a single 1 cc. portion of the sterilized water showed B. Coli.

Montreal, Quebec, draws its water supply from the St. Lawrence River and sterilizes it with hypochlorite. The untreated water averages 800 bacteria per cc., with B. Coli present in 98% of the 10 cc. portions and in 45% of the 1 cc. portions tested. The treated water averages 25 bacteria per cc., with B. Coli absent in both 10 cc. and 1 cc. portions tested.

Grants Pass, Oregon, has as its source of supply, Rogue River, a clear mountain stream. However, there are several sources of pollution by sewage from cities above. The hypochlorite treatment reduces the bacteria from an average of 600 to 15 per cc. Since the hypochlorite process was begun Sept. 16, 1911 and up to June 1, 1912, there were but two cases and no deaths from Typhoid Fever reported in this city of 5,000 inhabitants.

Baudette, Minn., had a Typhoid Fever epidemic in the Fall of 1910 and began immediately to sterilize the water supply. No specific data are available but the following quotation from a letter from the town clerk, is significant:—"It has been our experience that the hypochlorite plant is a very valuable asset. Previous to installing the hypo plant Typhoid Fever was very common. Since that time (to May 30, 1912) there has not been any Typhoid Fever called to our attention. We therefore believe that the hypo plant has been a very satisfactory preventative of this class of disease."

Nashville, Tenn., after drawing the water from the Cumberland River, coagulates it with Alum and allows it to settle in large basins. It is then sterilized with hypochlorite of lime. The average bacterial content of the raw water is 3,000 per cc., with 90% of the 1 cc. portions tested showing B. Coli present. The settled and sterilized water shows an average of only 70 bacteria per cc., and during the year 1910 only three samples out of 1,200 tested showed B. Coli present.

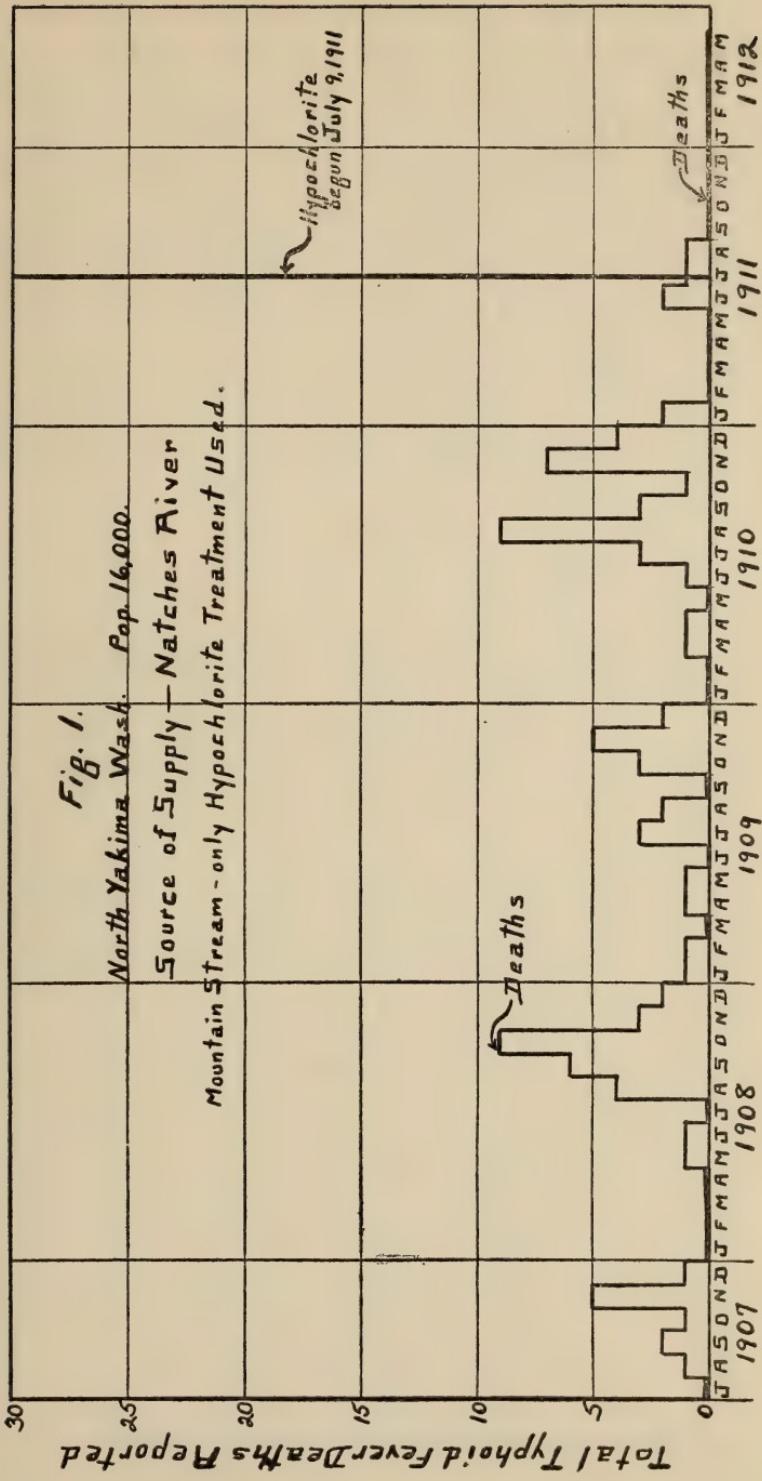


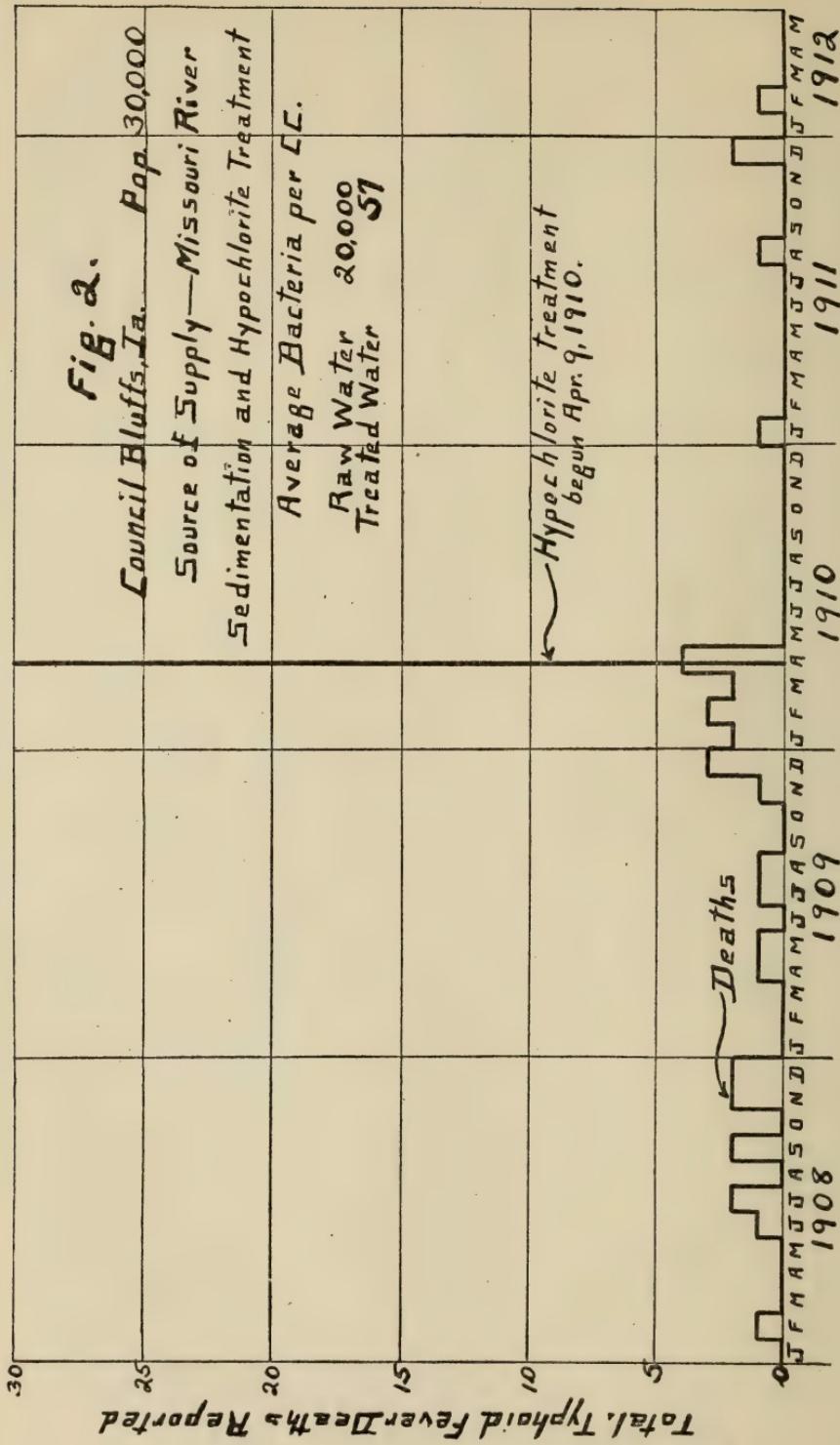
Fig. 2.

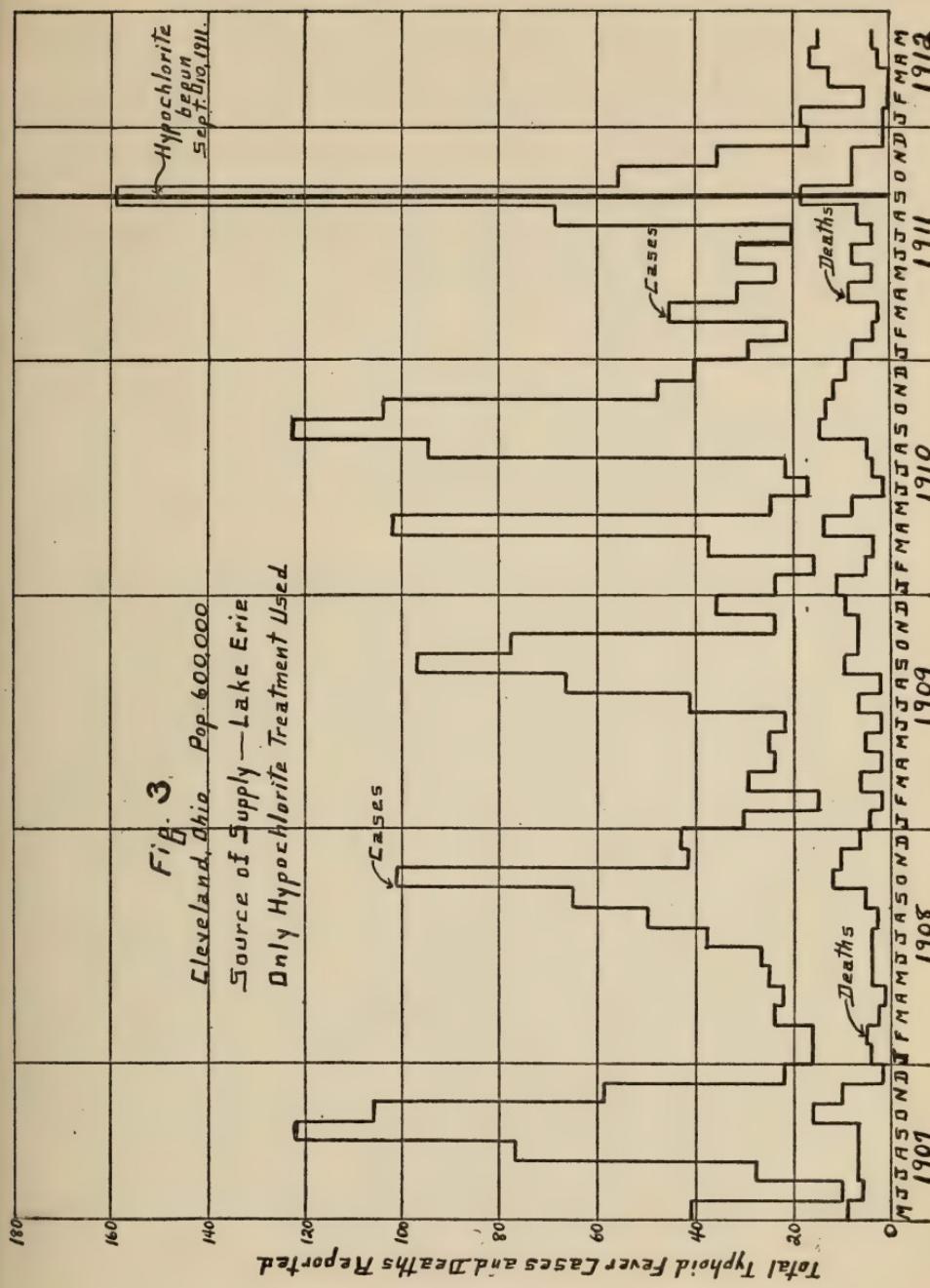
Council Bluffs, Ia. Pop. 30,000

Source of Supply—Missouri River
Sedimentation and Hypochlorite Treatment

Average Bacteria per CC.

Raw Water 20,000
Treated Water 57

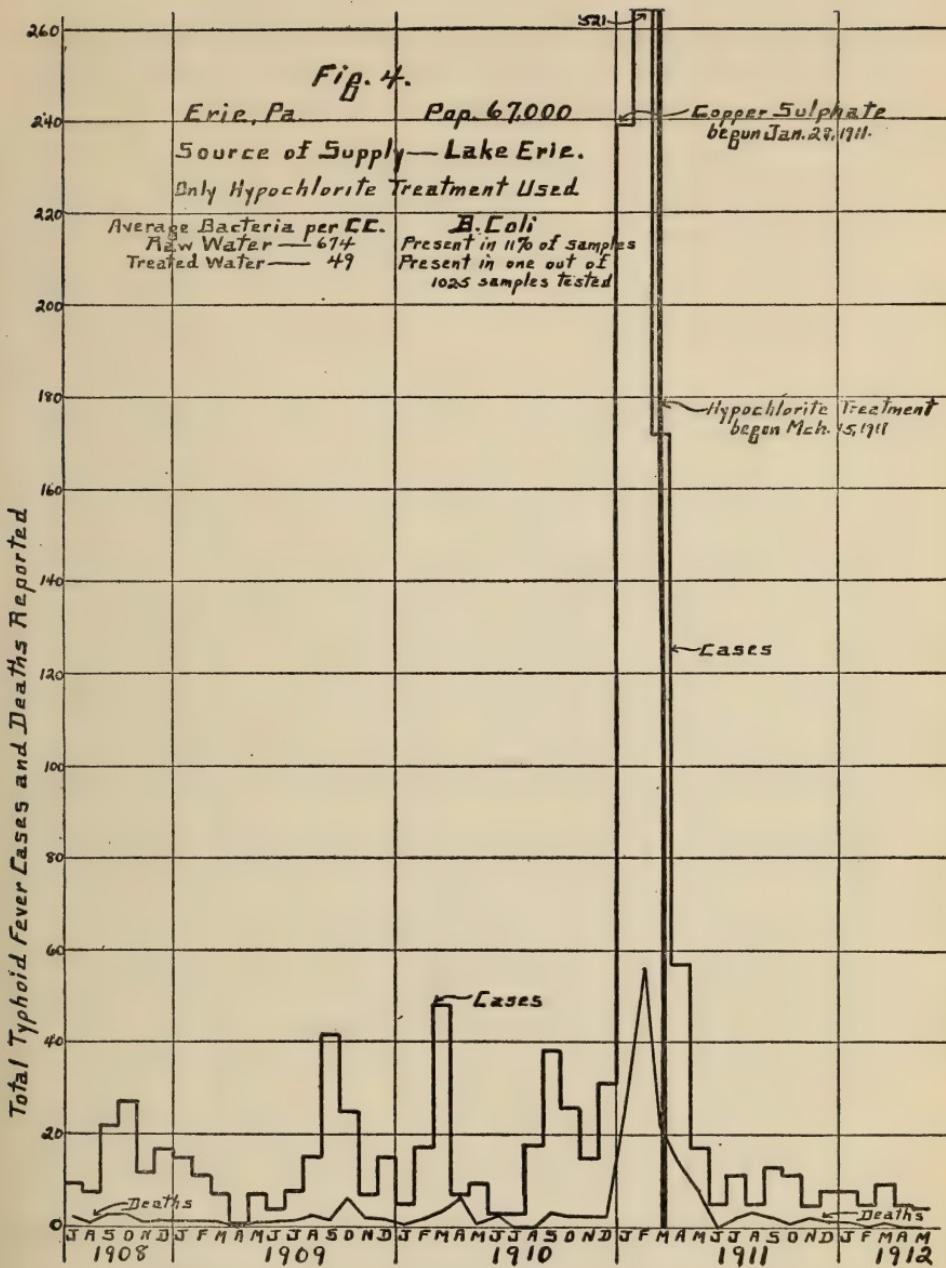




A comparison of Typhoid Fever statistics before and after the introduction of hypochlorite is very interesting. Typhoid Fever deaths in North Yakima, Wash., are shown in Fig. 1, covering a period of about five years. In 1910 there was an epidemic caused by a contamination to the domestic supply through a cross connection with a highly polluted fire service. During the period Sept. 1911 to June 1912 there was not a single death from Typhoid Fever and only one case was reported between Dec. 22, 1911 and June 1, 1912. The water sterilization began July 9, 1911. The source of supply is a mountain stream which is open to contamination. The reduction in the number of cases and deaths from Typhoid Fever is due in part to a general clean-up and condemnation of many polluted shallow wells as well as to the hypochlorite treatment in this booming city of the Northwest.

Fig. 2 shows the wonderful efficiency of hypochlorite in stopping a Typhoid Fever epidemic in Council Bluffs, Iowa, which began in the Fall of 1909 and ended with the introduction of hypo in April 1910. Since this treatment was inaugurated, a period of twenty-five months to June 1, 1912, there have been but five deaths from Typhoid Fever in this city with a population of 30,000 and one of these five deaths was that of an imported case. This is a remarkable record. For the eight months following the introduction of hypochlorite, there was not a single death from Typhoid Fever.

Fig. 3 shows the toll of Typhoid Fever cases and deaths in Cleveland, which draws its water supply from Lake Erie, which is polluted in part by its own sewage and in part by neighboring cities. Typhoid Fever has been prevalent to a great degree in this lake city for years and the diagram shows a remarkable reduction in the number of cases and deaths from this disease since the beginning of the treatment with hypochlorite in Sept. 1911. There were 159 cases and 19 deaths reported for that



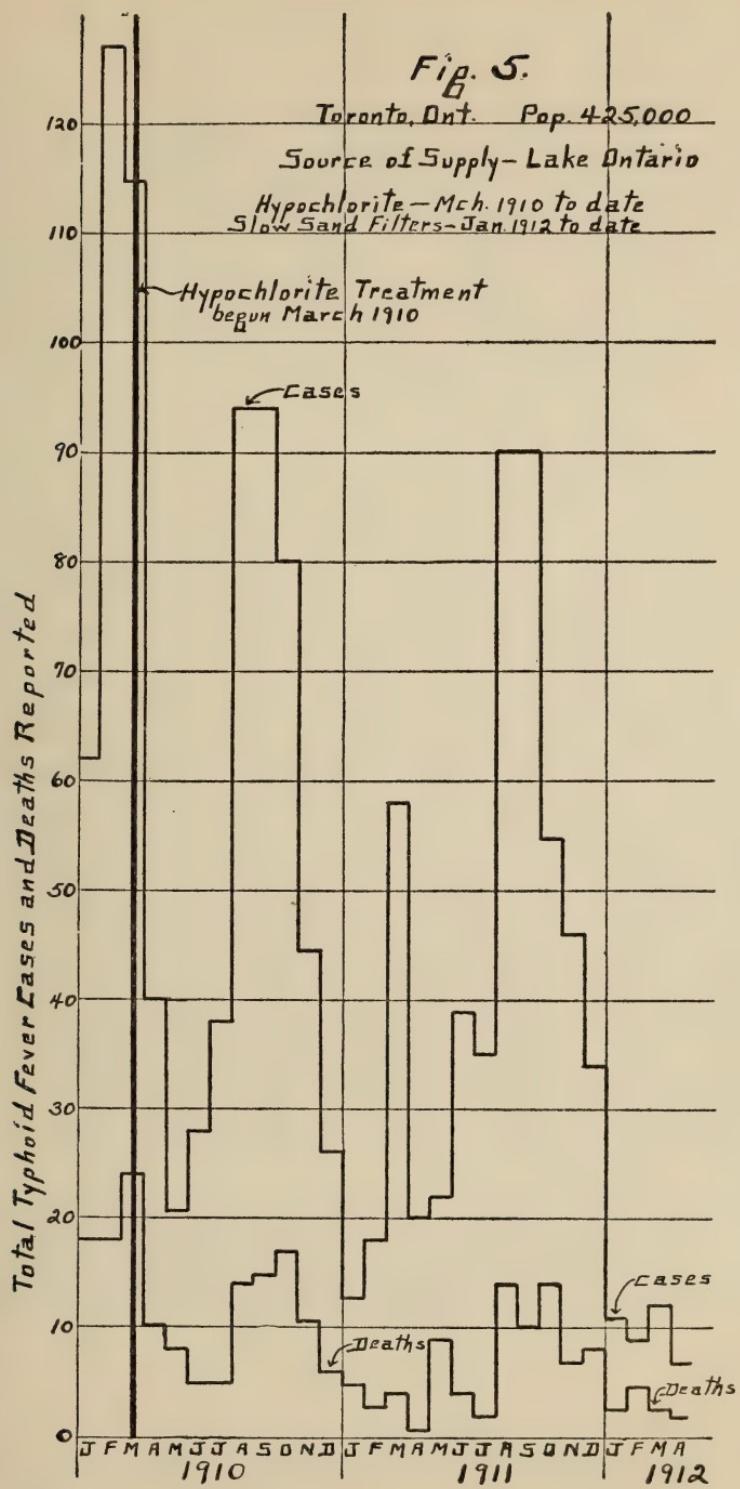
month. For the eight months Oct. 1, 1911 to June 1, 1912, there were totals of 180 cases and 28 deaths reported. During similar periods in previous years the figures are:—

| | | |
|------------------------------|-----------|-----------|
| Oct. 1, 1907 to June 1, 1908 | 290 cases | 46 deaths |
| " 1, 1908 " " 1, 1909 | 311 " | 52 " |
| " 1, 1909 " " 1, 1910 | 343 " | 66 " |
| " 1, 1910 " " 1, 1911 | 347 " | 65 " |
| <hr/> | | |
| Average 1907-1911 | 323 " | 57 " |

These figures compared with 180 and 28 cases and deaths respectively for 1911 to 1912, show reductions of 44% in the number of cases and 50.8% in the number of deaths. This represents an average of 29 fewer deaths in eight months while hypochlorite was being used compared with the period before the water was treated. Taking the figure of \$5,000 as the value of each life sacrificed to Typhoid Fever, the financial saving effected by hypochlorite in eight months has been \$145,000, which amount capitalized at 5% represents the tremendous sum of \$2,900,000.

Although it is acknowledged that the Typhoid epidemic at Erie was water borne, nevertheless the exact point of introduction of the contamination has not been definitely determined. The water supply is taken from Lake Erie and previous to March 15, 1911 was not treated with hypochlorite. Fig. 4 shows the Typhoid Fever statistics for a period of about four years. December 1910 with 31 cases and 2 deaths, was followed by January 1911 with 239 cases and 24 deaths. The Pennsylvania State Board of Health began treating the water supply with copper sulphate Jan. 28, 1911 and this was continued until the hypochlorite treatment was substituted. The latter process has been in use without cessation since March 15, 1911. The number of cases and deaths from Typhoid Fever during the twelve months from June 1 to May 31st., during the past four years is as follows:

| 1908-09 | | 1909-10 | | 1910-11 | | 1911-12 | |
|---------|--------|---------|--------|---------|--------|---------|--------|
| Cases | Deaths | Cases | Deaths | Cases | Deaths | Cases | Deaths |
| 153 | 16 | 202 | 29 | 1140 | 136 | 91 | 11 |



Thus it will be seen what a good record the hypochlorite treatment has made at Erie in the reduction of Typhoid Fever. The average number of cases and deaths for the three years 1908-1911 was 498 and 60, compared with 91 cases and 11 deaths since hypochlorite has been used. The value of 49 lives saved from Typhoid Fever at \$5,000 each, is \$245,000, which capitalized at 5% amounts to a total of \$4,900,000. The raw water averaged 674 bacteria per cc., with *B. Coli* present in 11% of the samples tested, while the treated water averaged only 49 bacteria per cc., with *B. Coli* present in only one sample out of 1025 examined—less than 0.1%.

Fig. 5 shows the Typhoid Fever statistics in the city of Toronto, Ontario. During the first two months of 1910 there were 723% more cases and 450% more deaths from Typhoid Fever than the average for the same two months during the five years previous. Hypochlorite treatment was begun in March 1910 and an immediate reduction in the number of cases and deaths was effected as shown in the curves. The cause for the curve for cases rising to 90 for two consecutive months is explained in a quotation from a letter from Dr. Geo. G. Nasmith, Director of Municipal Laboratories:—"I may say that last year our intake plugged with sand and we were forced to short circuit our water supply and take it from the bay into which all our sewage empties. We had the makings of the largest Typhoid epidemic ever known on this Continent but fortunately we had hypochlorite to depend on and we came through with a Typhoid death rate of 20 per 100,000 in 1911 as compared with 45 per 100,000 in 1910, which you will agree, was an extremely satisfactory showing." The first four months of 1912 show 64% fewer cases reported than the same period in 1911 and 65% fewer cases than the average for the same periods 1905 to 1910 inclusive and 50% fewer deaths.

Baltimore, Md., drawing its water supply from two impounding reservoirs, began to sterilize the water with hypochlorite June 6, 1911 to keep down the annual Autumn Typhoid Fever epidemic.

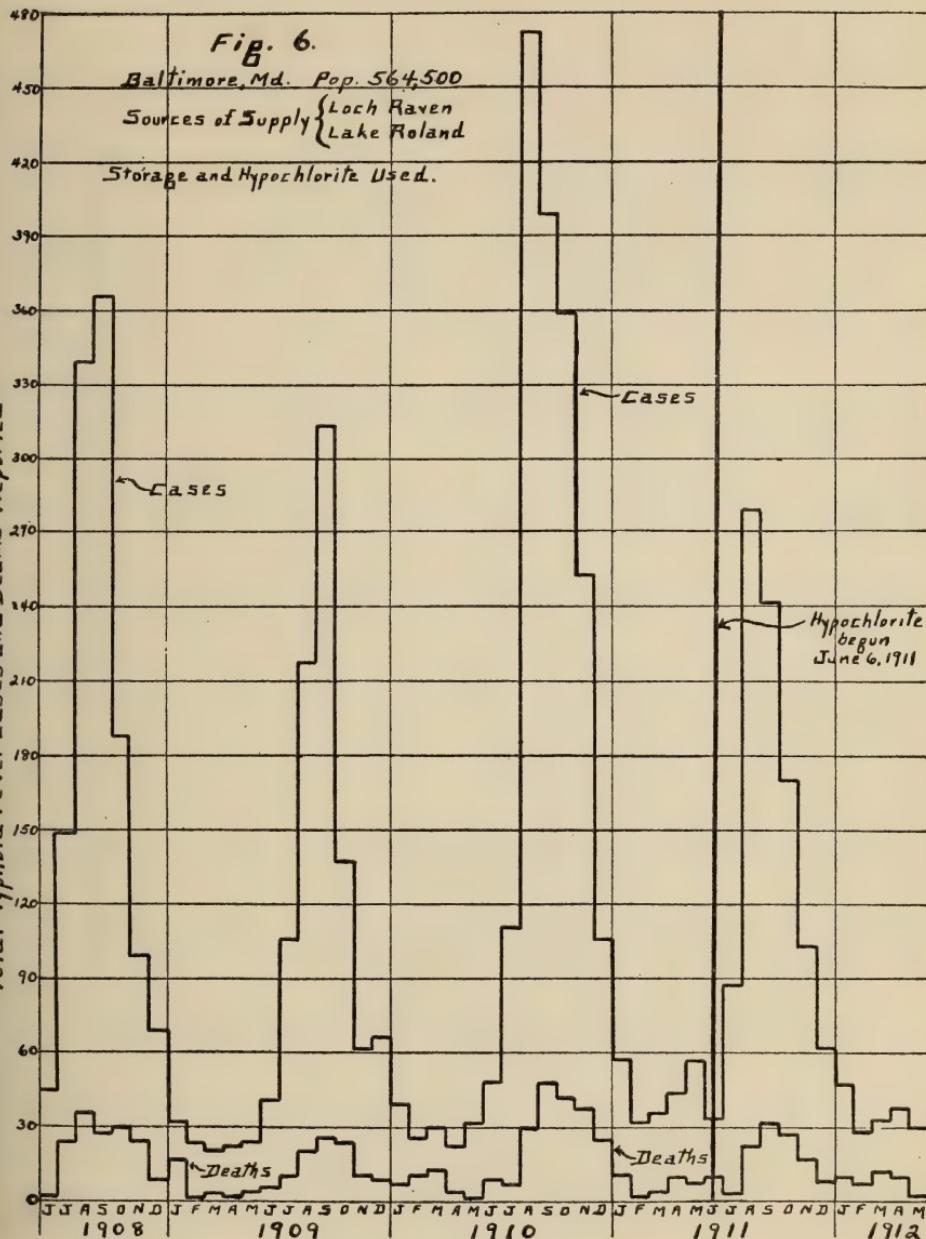
Fig. 6.

Baltimore, Md. Pop. 564,500

Sources of Supply { Loch Raven
Lake Roland

Storage and Hypochlorite Used.

Total Typhoid Fever Cases and Deaths Reported



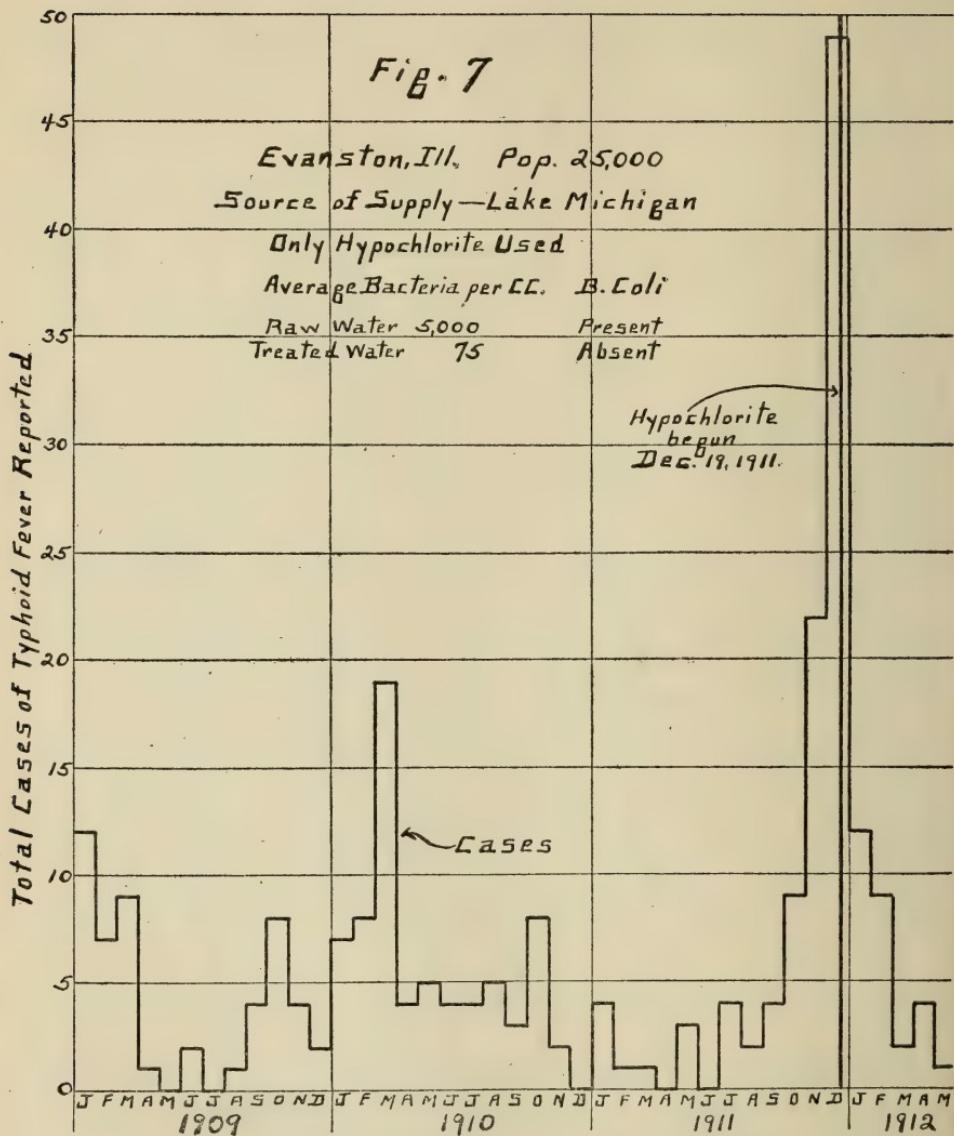
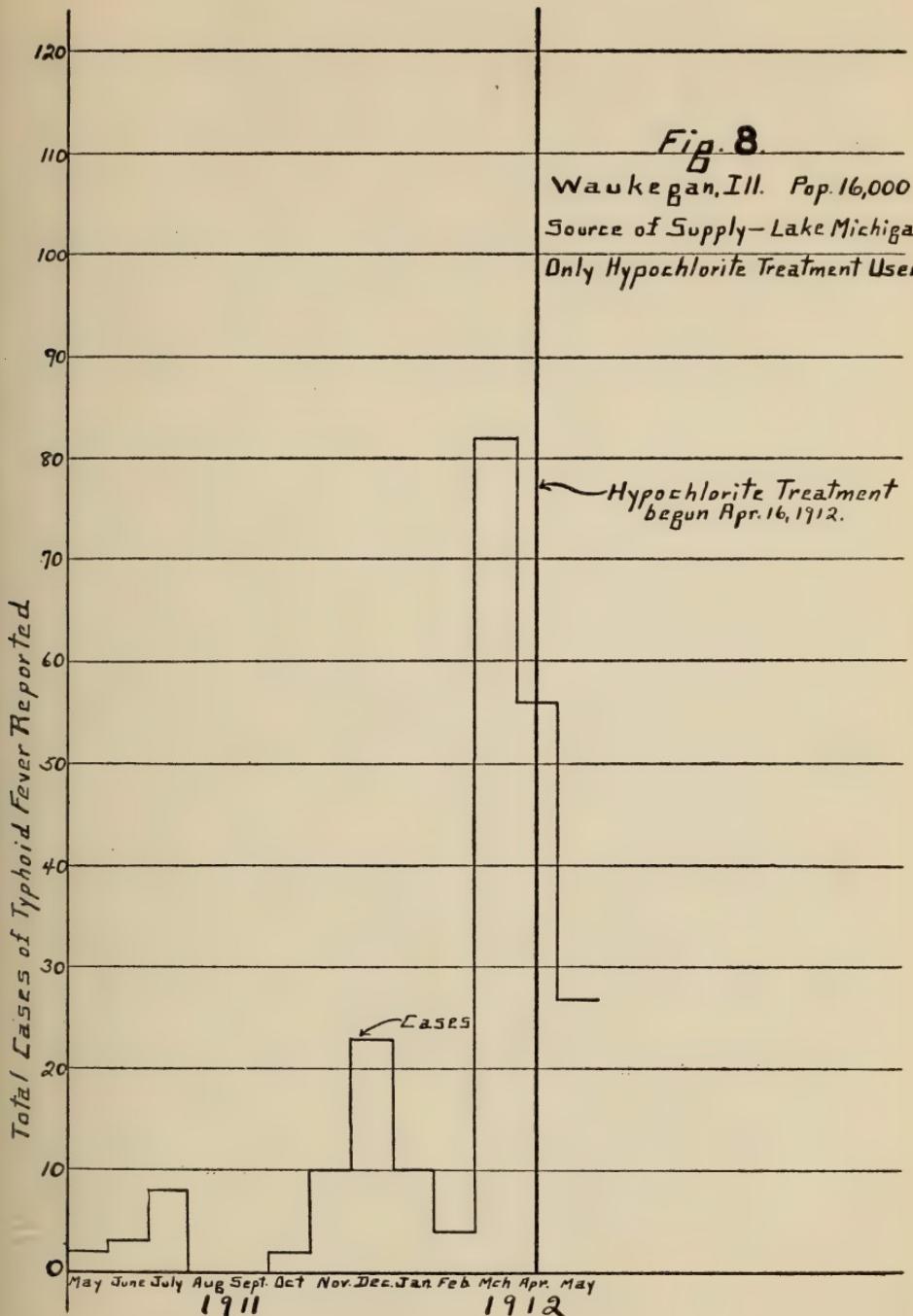


Fig. 8.

Waukegan, Ill. Pop. 16,000
Source of Supply—Lake Michigan
Only Hypochlorite Treatment Used



How well this treatment succeeded is shown in Fig. 6. Both the curves for cases and deaths are lower than before the use of hypochlorite. For the period June 1, 1910—May 31, 1911, there were 1964 cases and 233 deaths from Typhoid Fever, while from June 1, 1911 to May 31, 1912, while using hypochlorite, there were only 1155 cases and 160 deaths, reductions of 41% and 31% respectively. Hypochlorite treatment presumably saved 73 lives in one year. These valued at \$5,000 each, amount to \$365,000, which totals the enormous sum of \$7,300,000 when capitalized at 5%. This is a wonderful saving to a community of 564,000 people in 12 months.

During the past Winter Evanston, Ill., had a Typhoid Fever epidemic traceable to the water supply, contaminated by the sewage of the city itself. Fig. 7 shows the beneficial effect of the hypochlorite treatment in stopping the epidemic. Although the sterilizing of the water was not begun until Dec. 19, 1911, nevertheless there was a reduction from 49 cases reported in Dec. 1911 to 12 cases in Jan. 1912, which dropped still further to 9 cases in February, showing how thoroughly the hypochlorite treatment did its work. The untreated lake water averaging 5,000 bacteria per cc., with *B. Coli* present, was reduced to an average of 75 per cc., with *B. Coli* shown to be absent in all 1 cc. portions tested.

At Waukegan, Ill., conditions as to the pollution of the city water supply with the city's own sewage, are identical with those at Evanston. The increase in Typhoid Fever cases reported however, occurred later than in Evanston. Fig. 8 shows the number of cases reported before and after the introduction of the hypochlorite treatment. It will be seen that 82 cases in March were reduced to 56 in April and 27 in May, hypochlorite having been used for the first time on April 16, 1912.

At Minneapolis, Minn., there was an abnormal amount of Typhoid Fever in 1909 and 1910. The water supply was taken from the Mississippi River without any treatment. The use of hypochlorite was begun late in 1910 and has been continued

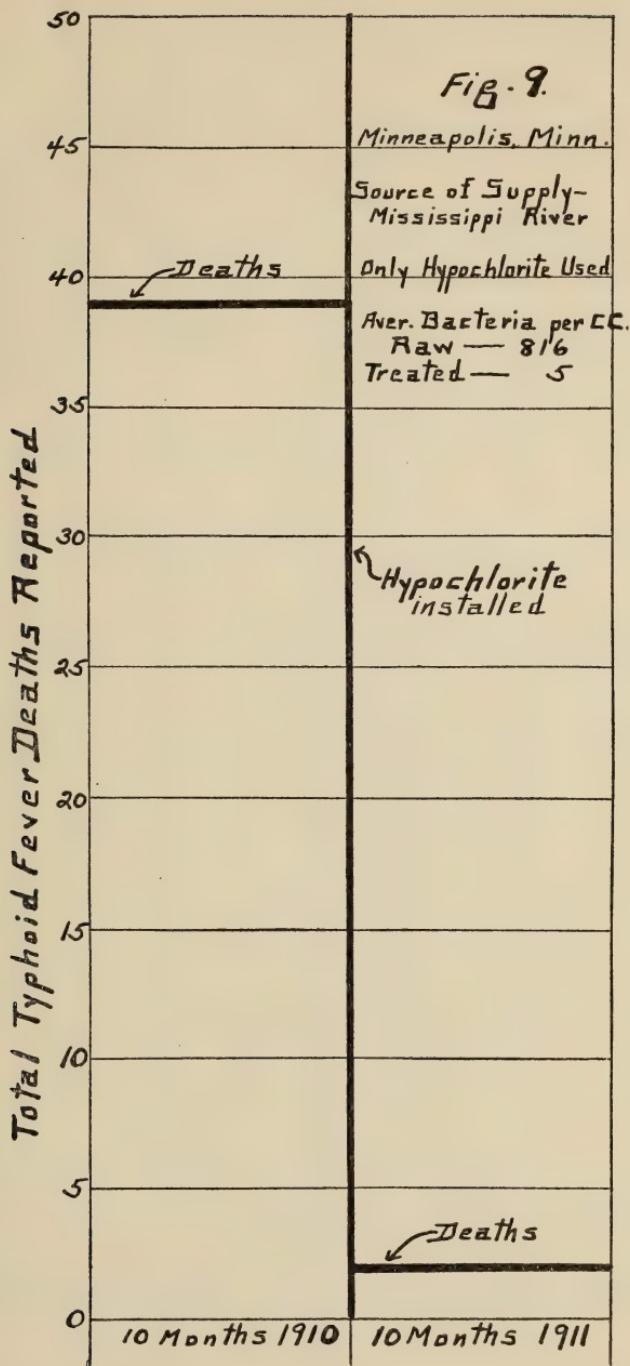


Fig. 10.

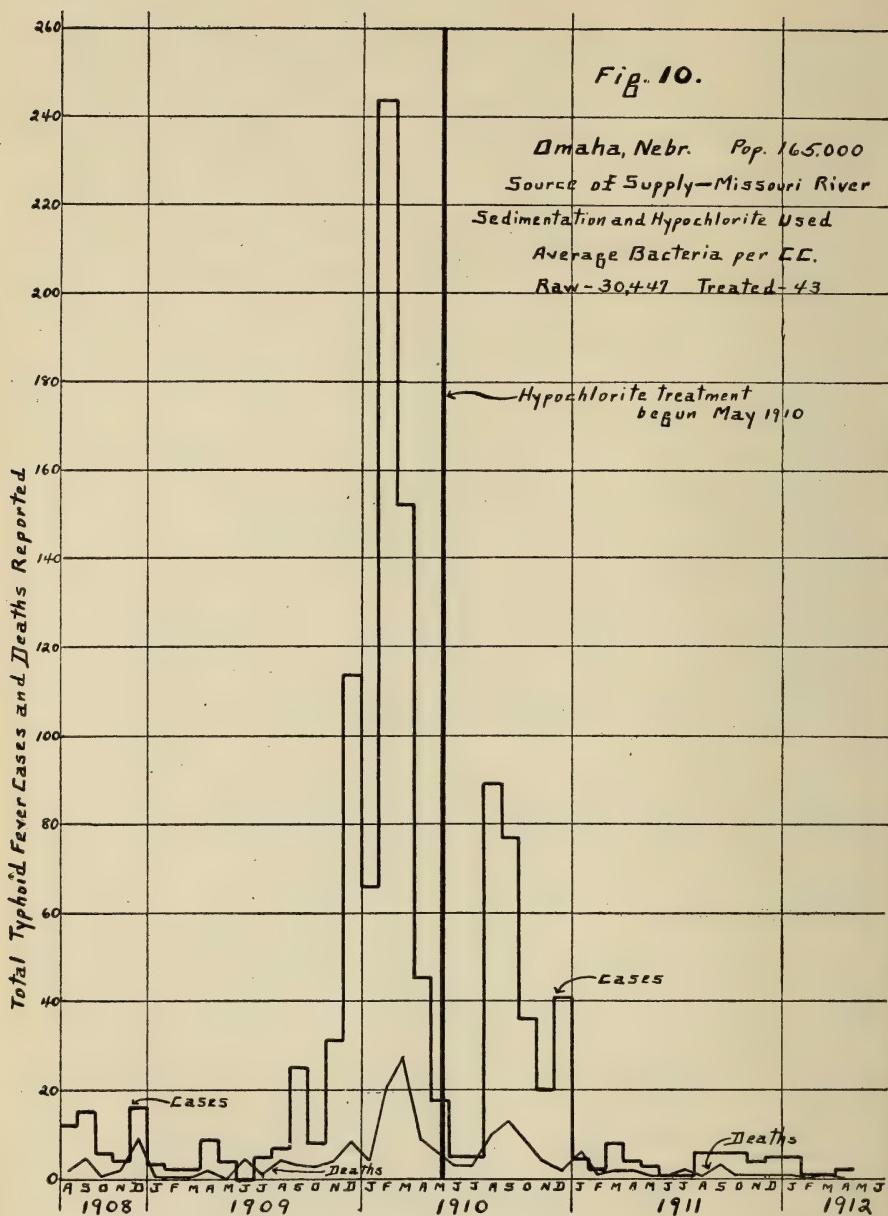
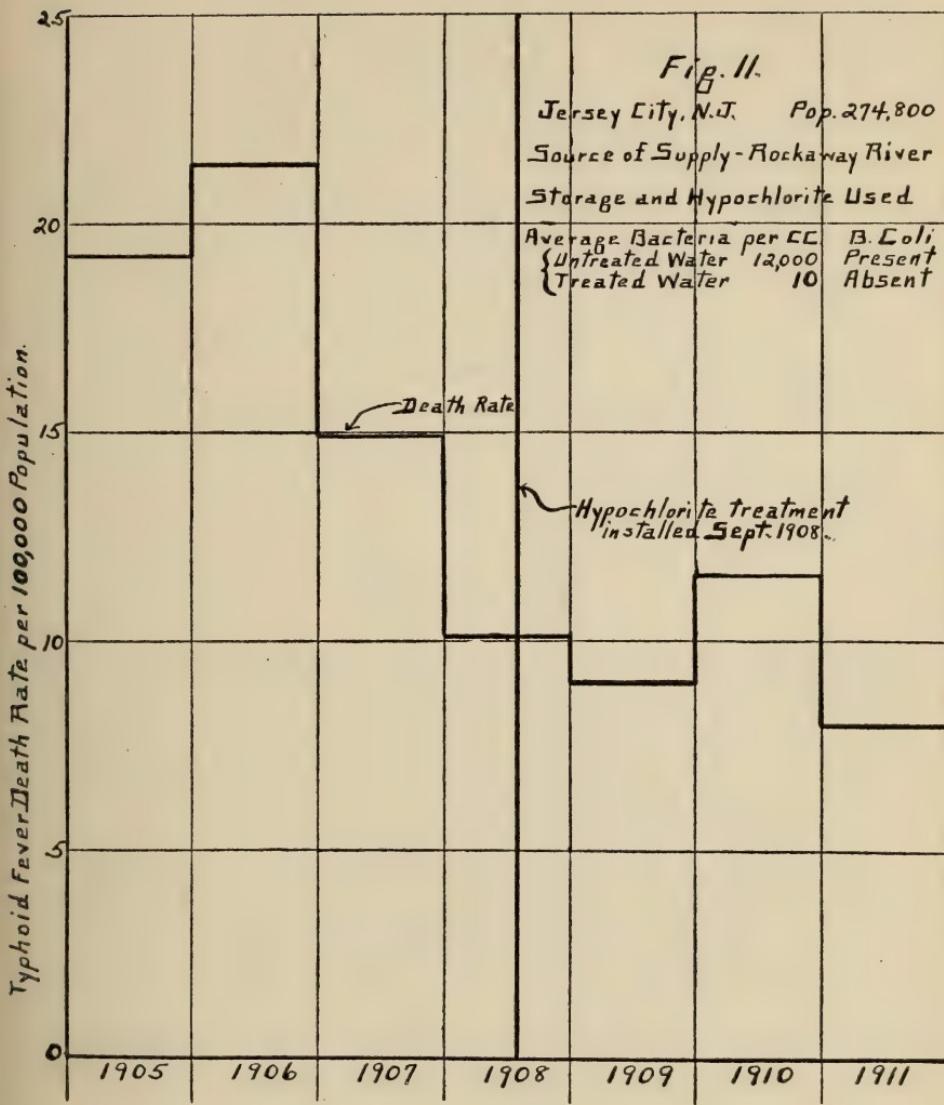


Fig. II.

Jersey City, N.J. Pop. 274,800
Source of Supply - Rockaway River
Storage and Hypochlorite Used

Average Bacteria per CC
{ Untreated Water 12,000
Treated Water 10

B. Coli
Present
Absent



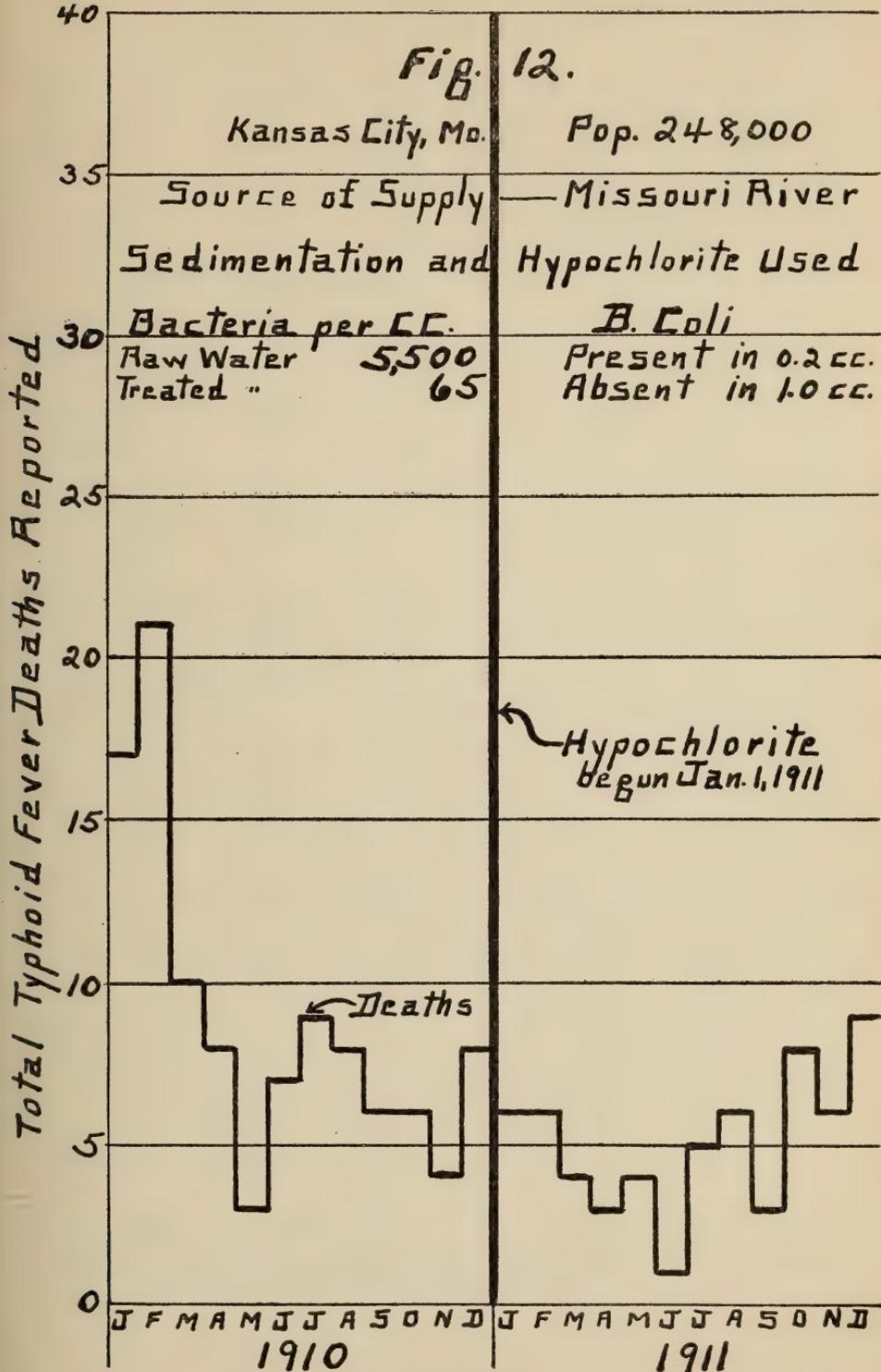
without interruption since that time. A modern filter plant of the rapid sand type is now being constructed but the sterilizing process will be used in conjunction with it when completed. The water is reduced from an average of 816 bacteria per cc. to 5 per cc. Fig. 9 shows graphically the enormous reduction in Typhoid Fever deaths reported during the ten months following the adoption of the hypochlorite treatment, showing also the number of deaths for the ten months previous. These figures are 39 deaths before hypochlorite and only 2 after hypochlorite was installed, a reduction of 95%. This is remarkable.

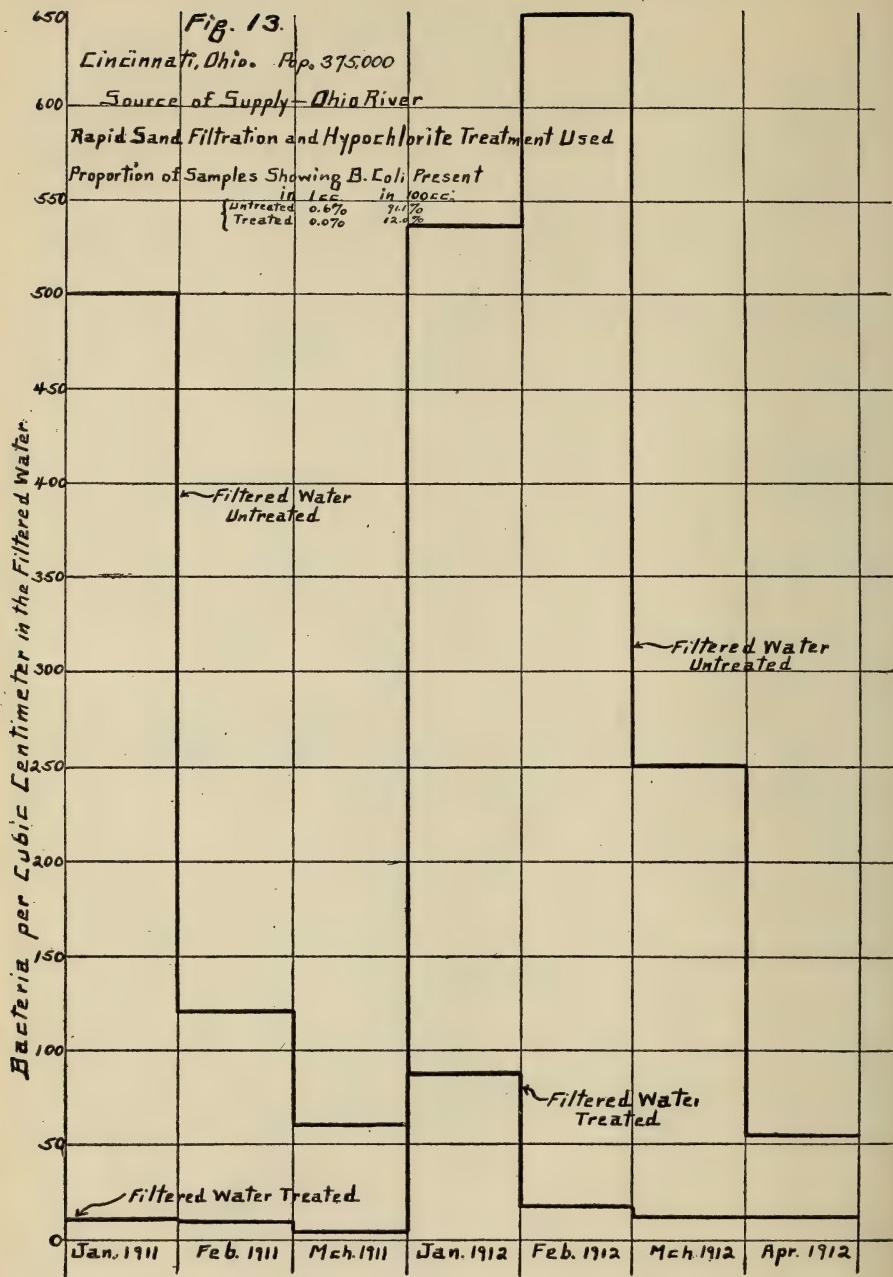
Omaha, Neb., has used the hypochlorite treatment since May 1910, at which time there was an epidemic of Typhoid Fever in the city. The results have been wonderful. Fig. 10 gives a striking diagram showing the results. A comparison of the curve for 1911 and 1912 with previous years, especially 1910, shows a remarkable reduction. The Typhoid Fever death rates per 100,000 for Omaha have been:—

| 1908 | 1909 | 1910 | 1911 |
|------|------|------|------|
| 16 | 26 | 67 | 13 |

A reduction from 67 to 13 per 100,000 is remarkable and it is difficult to say how much higher the rate would have been in 1910 had not the sterilizing process been installed in May of that year. It is worthy of mention that the treated and settled water shows an average of only 43 bacteria per cc., whereas the raw water from the Missouri River averages 30,477 per cc.

Jersey City, N. J., was one of the first cities to adopt the hypochlorite treatment for municipal water supplies. The water from the storage reservoir averages 12,000 bacteria per cc., with *B. Coli* present but the treated water averages only 10 per cc., with *B. Coli* absent. Fig. 11 shows the Typhoid Fever death rates per 100,000 for a period of seven years, the hypochlorite treatment having been installed in Sept. 1908. The



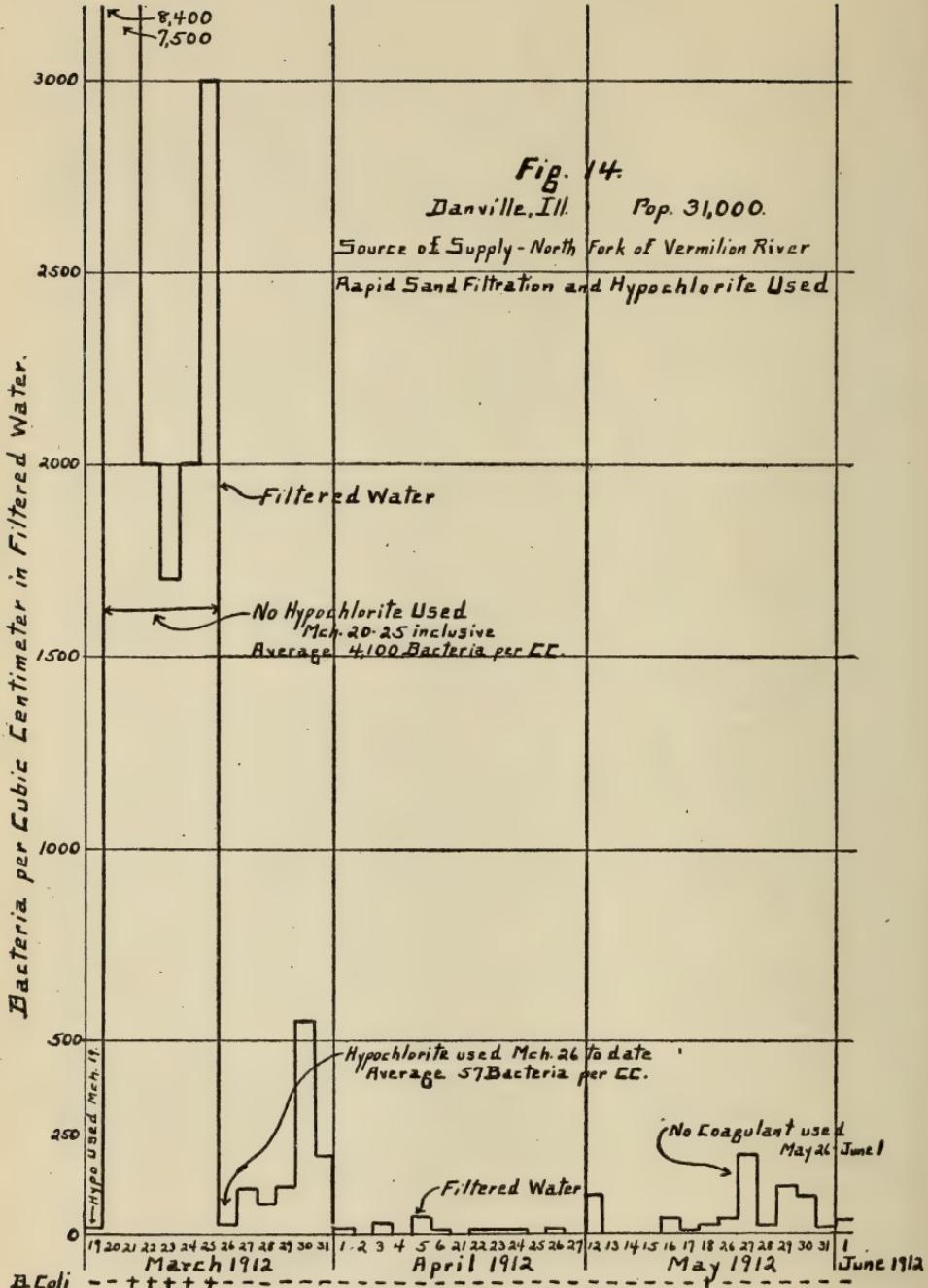


average for 1905, 1906 and 1907 is 18.5 per 100,000 and this is reduced to an average of 9.6 per 100,000 for the three years following the use of hypochlorite, namely 1909, 1910 and 1911, a reduction of 48% in the average Typhoid Fever death rate.

Kansas City, Mo., takes its water supply from the muddy and polluted Missouri River and by means of sedimentation and sterilization reduces the bacterial content from an average of 5,500 per cc., to 65 per cc. The raw water shows *B. Coli* present in .2 cc., whereas this sewage organism is absent in all 1 cc. portions of the treated water tested. Fig. 12 shows the total number of deaths reported monthly during 1910 without sterilization of the water and for 1911 with hypochlorite treatment in use. The number of deaths was reduced from 107 to 61 or 43%. Many people in Kansas City use the clear and sparkling waters that issue in many places from springs and which can be pumped from surface wells. These waters have been shown to be very highly contaminated, although they are of very attractive appearance. The city is now conducting a campaign to discontinue the use of these waters for drinking.

Cincinnati, Ohio has a rapid sand filter plant with a capacity of 112,000,000 gal. per day. The hypochlorite treatment has been used as an adjunct to the filtration process since Dec. 1910. In Fig. 13 is shown the reduction in bacteria in the filtered water by means of the hypochlorite treatment, a reduction from an average of 315 to 26 per cc., or 91.7% reduction in the filtered water itself. *B. Coli* was present in 0.6% of the 1 cc. samples and in 91.1% of the 100 cc. samples of filtered water examined but in the treated filtered water tested no 1 cc. portions showed *B. Coli* present and only 12% of the 100 cc. portions were positive.

Although Danville, Ill., has been using the hypochlorite treatment as an adjunct to their rapid sand filter plant only for a very short time, (since Feb. 1912), nevertheless the bacterial data



on the filtered water, plotted in Fig. 14, are very interesting. An examination of this curve will show that during the time that hypochlorite was used, the average bacterial content of the sterilized filtered water was only 57 per cc. During the period from March 20-25 inclusive, the supply of hypochlorite was exhausted and so none was used. The bacterial content of the untreated filtered water during this period was 4,100 per cc. With hypochlorite treatment in use March 19th., the count was but 20 per cc., on March 20th., without Hypochlorite, the count jumped up to 8,400 per cc. The removal by filtration without sterilization, from the raw water averaging 57,000 bacteria per cc., was 93.9%; by filtration and sterilization from the raw water averaging 52,496 bacteria per cc., the removal was 99.89%. Without sterilization, *B. Coli* was present in the filtered water on five of the six days; with sterilization, *B. Coli* was present on one day out of 34. The turbidity of the raw water was so low from May 26 to June 1, 1912, that no coagulent was used and only hypochlorite added to the filtered water. The average reduction in bacteria during this period was 99.6%.

These data show conclusively that the hypochlorite of lime treatment of water supplies is wonderfully effective, that it reduces the bacterial content of water to a very low number, that it practically eliminates *B. Coli* and therefore, we think, *B. Typhosus*, from water supplies, that it is a very valuable adjunct to filter plants, that mountain streams and impounded reservoir supplies are made safe by its use, that it has stopped many Typhoid Fever epidemics already begun and in all probability it has prevented many epidemics from occurring. Hypochlorite is not a panacea for all troubles arising from water supplies but when properly applied to the proper water in the correct quantities, it will accomplish wonderful results. Its great cheapness as to installation and operation, the short time necessary to install the treatment and its comparative simplicity, will surely cause sterilization by hypochlorite of lime to be continued and to be adopted by other cities where the supply is not all that it should be.

THE RATIONAL USE OF DISINFECTANTS AND ALGICIDES IN MUNICIPAL WATER SUPPLIES

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The axiomatic necessity of providing any city or social community with potable water has brought forth many types of standards for determining the suitability of a given source of supply. The old beliefs, still held by many chemists and water engineers, lay great emphasis upon those sources of water which are intrinsically pure and attractive; the deep well and the supply carried from barren or scantily populated mountain peaks being the two ideals. While such sources may be desirable, to suppose that they may be secured by all cities of the country is but a vision of the impractical dreamer. Obviously the mountains of this country are not available to the greater portion of our inhabitants, nor is it often feasible to secure from wells the quantity of water needed for a centralized distribution to a congested populated.

The use of surface water, taking precautions to assure its safety and potability, becomes the only compromise between what is perhaps desirable and what is physically possible. Some of the advocates of natural purity as the criterion of a good water insist that since a compromise of this character must be made, the precautions necessary for changing a polluted source of supply into a safe one must resemble closely the methods of purification existing in nature. They therefore disapprove of the employment of algicides and disinfectants as well as the use of the precipitation or coagulating chemical agents employed in what is usually termed the mechanical system of filtration.

I believe it is more reasonable to regard modern municipal water as an artificial product which can best be prepared for domestic use by frankly artificial means. Three important factors must then be considered: first, the quality of the product (meaning the safety, appearance, taste, hardness, etc.) at the

point of delivery to the consumers; second, the certainty of the methods for securing and maintaining a water of desirable quality; and, third, the cost of these methods.

It is unfortunate that questions of cost should be of paramount importance in sanitary developments; all practical affairs are similarly limited, however, and our greatest value to society at large will result from demonstrating that certain sanitary improvements are desirable and that the improvements are such that their cost is within the limit which the community can and should afford. In urging sanitary reforms we must remember that water supplies should be considered community problems. "There can be no doubt that the responsibility of furnishing pure water should fall exclusively upon the company or municipality controlling the water supply, but the degree to which the adjacent sewage disposal plants should aid in protecting a source of supply from pollution should be determined by some unprejudiced central authority.¹

With the rapidly increasing urban population of this country it is certain that filtration alone is seldom an assurance of safe water. Under practical conditions a filtration system of any type whatever can but reduce, it can not remove, the dangers of a water supply which is continuously subjected to excessive sewage pollution. Filtration should therefore be regarded chiefly as a means for improving the appearance and usefulness of water. In addition some one of the available methods of disinfection must be employed to remove the danger of a possible pollution. Ozone, ultra violet rays, hypochlorites of various origins, copper sulphate, and perhaps other salts may be useful. The excellent results obtained from the use of hypochlorite first at Boonton by Johnson² and later in other localities, together with the adoption by the Minnesota State Board of Health³ and the Indiana

¹ Kellerman, Karl F., Pratt, R. Winthrop, and Kimberley, A. Elliot, *The Disinfection of Sewage Effluents for the Protection of Public Water Supplies*. Bulletin 115, Bureau of Plant Industry, U. S. Department of Agriculture, p. 8, 1907.

² Johnson, Geo. A., *Water Sterilization at Boonton, N. J.* Municipal Engineering, Vol. 37, No. 3, p. 158-161, 1909.

³ Childs, J. A., and Whittaker, H. A., *The Traveling or Portable Hypochlorite Water-Disinfecting Plant of the Minnesota State Board of Health*. Engineering News, Vol. 65, No. 14, p. 402-403, 1911.

State Board of Health¹ of hypochlorite for their temporary emergency disinfection outfit for water supplies, show that at present this agent must be considered the most practical as well as the most desirable disinfectant. Opinions will differ regarding the conditions under which disinfection of a supply is desirable. I urge that provision should be made for occasional disinfection of all supplies except those whose sources assure continued purity; and that continuous disinfection should be practiced for all supplies constantly subjected to dangerous pollution.

The usefulness and hence the actual value of even a safe water may be greatly reduced, as Whipple² has pointed out, through the occurrence of disagreeable tastes and odors. This deterioration is almost always due to the growth of algae or fungi in the reservoir, lake, or river, or even in the pipelines themselves. Since 1904 copper sulphate has been used to eradicate or to reduce the development of these troublesome organisms, and the method of copper treatment³ outlined in 1904 and 1905 has been not materially changed. The large number of samples from ill-smelling water supplies sent to me for identification and advice as to treatment has enabled me to tabulate the occurrence of the more troublesome species, as well as to determine suitable treatment for each of these.

The following table shows the occurrence by States of the twelve genera of algae most frequently reported to me during the past eight years as troublesome. The use of copper sulphate for the control of these algal pollutions has now been thoroughly tested, and I believe this method should be adopted wherever tastes and odors in water are caused by algae.

¹ Emergency Hypochlorite Plant. Municipal Journal, Vol. 32, No. 25, p. 937, 1912.

² Whipple, Geo. C., *The Value of Pure Water*, p. 39. New York, 1907.

³ Moore, Geo. T., and Kellerman, Karl F., *A Method of Destroying or Preventing the Growth of Algae and Certain Pathogenic Bacteria in Water Supplies*. Bulletin 64, Bureau of Plant Industry, U. S. Department of Agriculture, 1904.

Moore, Geo. T., and Kellerman, Karl F., *Copper as an Algicide and Disinfectant in Water Supplies*. Bulletin 76, Bureau of Plant Industry, U. S. Department of Agriculture, 1905.

TABLE SHOWING THE OCCURRENCE OF GENERA OF ALGAE MOST
FREQUENTLY REPORTED AS CAUSING TROUBLE IN RESER-
VOIRS AND PONDS

For the convenience of those who wish to superintend personally the treatment of water for removing algal pollutions, I have prepared tables showing the quantity of copper sulphate required to eradicate the more common forms, and also the concentration beyond which copper sulphate may be dangerous for several kinds of fish.

TABLE SHOWING QUANTITY OF COPPER SULPHATE REQUIRED TO KILL VARIOUS FORMS OF ODOR-PRODUCING ORGANISMS

Copper sulphate expressed as parts per million

| | | | | |
|-----------------|----------|----------------|---------|-----|
| Anabaena, | .09 | Kirchneriella, | 5.00 to | 10 |
| Asterionella, | .10 | Leptomitus, | .40 | |
| Beggiatoa, | 5.00 | Microspora, | .40 | |
| Chara, | .20 to 5 | Navicula, | .07 | |
| Cladophora, | 1.00 | Oscillatoria, | .10 to | .40 |
| Cladothrix, | .20 | Peridinium, | 2.00 | |
| Clathrocystis, | .10 | Scenedesmus, | 5.00 to | 10 |
| Coelosphaerium, | .30 | Spirogyra, | .05 to | .30 |
| Conferva, | .40 to 2 | Ulothrix, | .20 | |
| Crenothrix, | .30 | Uroglena, | .05 | |
| Euglena, | 1.00 | Volvox, | .25 | |
| Fragillaria, | .25 | Zygnema, | .70 | |
| Hydrodictyon,, | .10 | | | |

TABLE SHOWING SAFE LIMIT FOR TREATING WATER WITH COPPER SULPHATE WHEN CERTAIN FISH ARE PRESENT

Copper sulphate expressed as parts per million

| | | | |
|-------------|------|-----------|------|
| Black bass, | 2.10 | Pickerel, | .40 |
| Carp, | .30 | Suckers, | .30 |
| Catfish, | .40 | Sunfish, | 1.20 |
| Goldfish, | .50 | Trout, | .14 |
| Perch, | .75 | | |

(*Abstract*)

THE USE OF HYPOCHLORITE IN CHECKING A MILD
TYPHOID EPIDEMIC AT EVANSTON, ILL.

W. LEE LEWIS.

Evanston, Ill.

1. A typhoid rate in the City of Evanston, Illinois, twice that of neighboring Chicago for a number of years is explained by the absence of sewage diversion in the former city.

2. Evanston's financial inability to independently use the north branch of the drainage canal to secure which it entered the "Sanitary District" and for which it has been heavily taxed, brings up a new problem of jurisdiction.

3. A mild typhoid epidemic of last winter was obviously water born, as the time of the year, a study of the individual cases and the tests upon the water indicated.

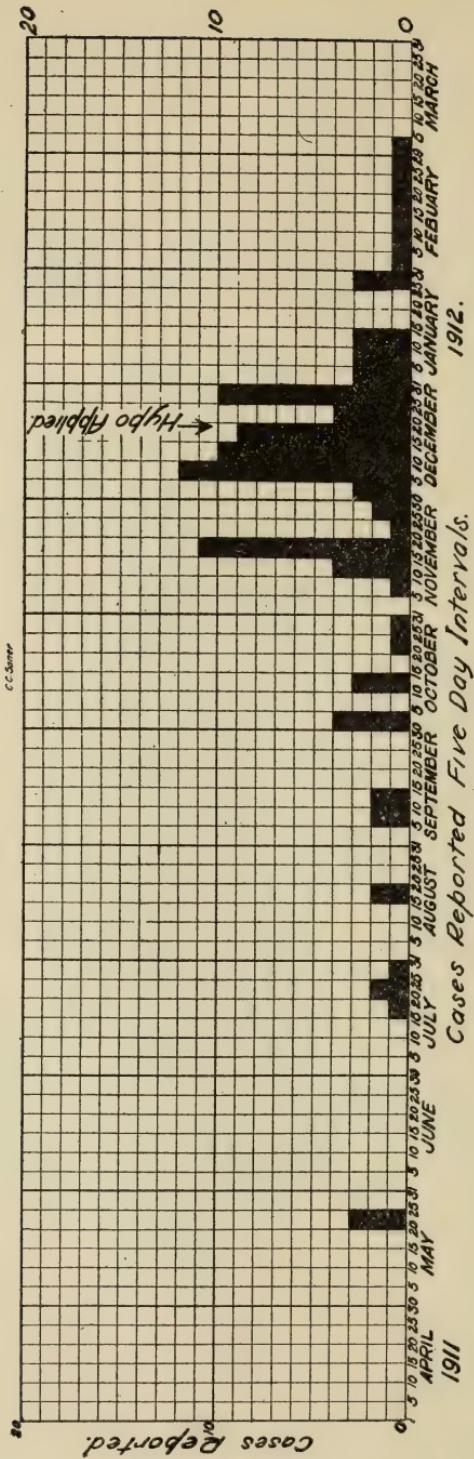
4. A hypochlorite plant rapidly and economically installed checked the epidemic in a rational manner and has continued to keep the typhoid rate for the city well with the present limit of "residual typhoid" for this country.

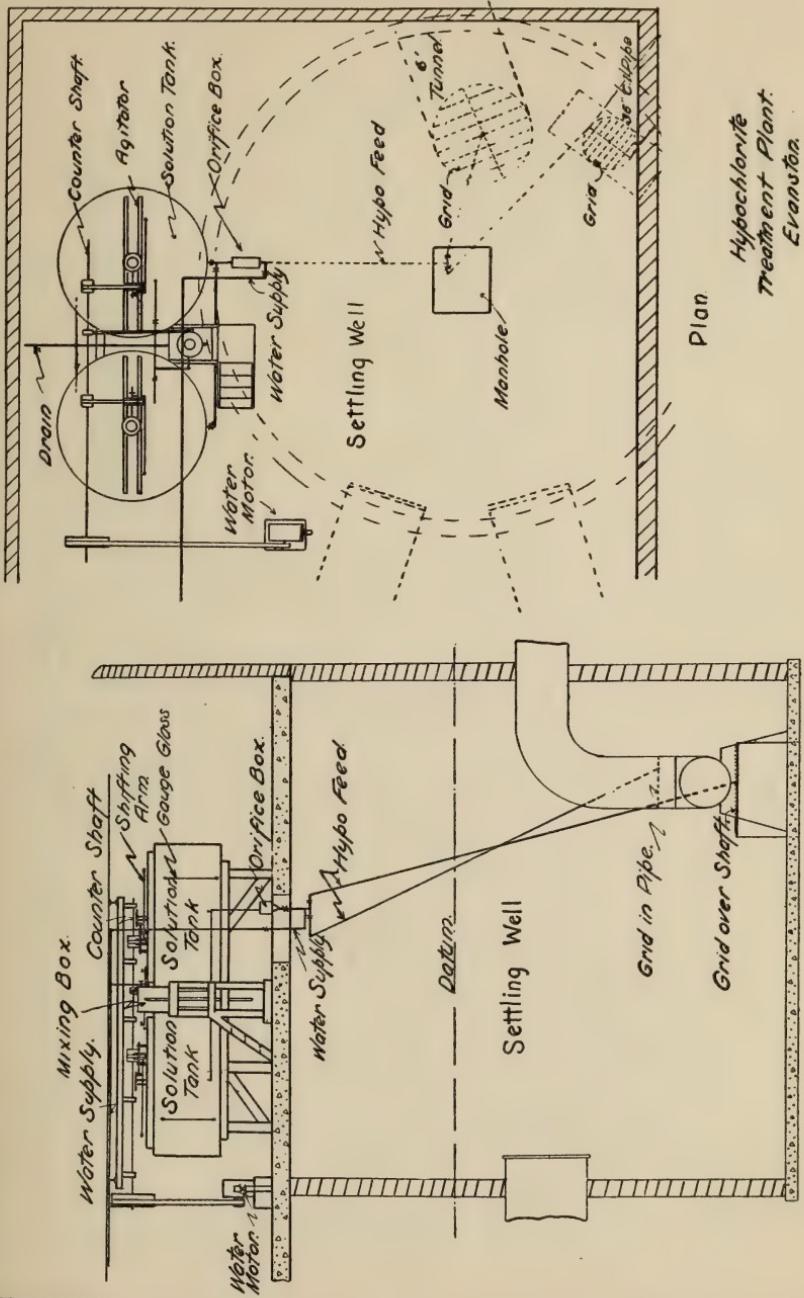
5. The results were not accomplished without some complaints just and unjust from the consumers.

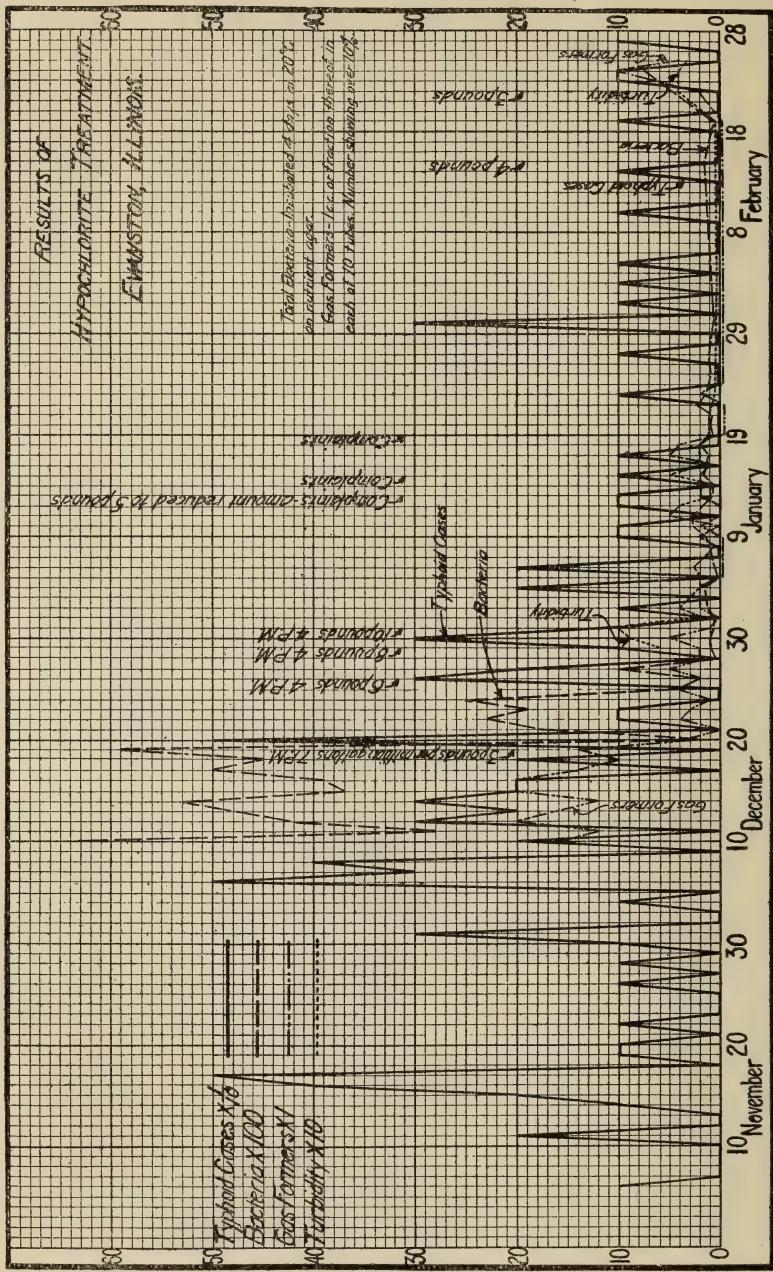
6. Preliminary laboratory experiments were no criterion of the action of the chemical under practical conditions, and brought out some interesting suggestions as to the ability of gas producers to revive within a certain time after "Hypo" treatment.

7. The treatment has on the whole been eminently satisfactory though by no means regarded as a permanent solution of the local problem.

TYPHOID CHART.
EVANSTON.







BIO-CHEMISTRY OF SEWAGE

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In an earlier paper¹ the writer has dealt with the question of the interpretation of a sewage analysis. Such an interpretation in its fullest sense would involve a complete statement of the physical, chemical and biological properties of a sewage as indicated by the ordinary analytical results. It was shown that the analytical figures usually obtained did not provide sufficient information to permit of any such thorough interpretation. The problem was therefore somewhat simplified by first defining three groups of characteristics of a sewage and attempting to correlate them with the analytical features. These three general properties of a sewage may be briefly defined as follows:-

The physical property of concentration refers simply to what is ordinarily known as the strength of the sewage. The chemical property of composition refers to the type or kind of sewage. For example, the wastes of the various manufacturing industries differ from one another and from domestic sewage in composition. The third characteristic is the bio-chemical one which was called the condition of the sewage. This is in large measure independent of the other two and is determined by such factors as age, temperature, and biological activity.

In the paper referred to especial attention was given to the first two groups of characteristics, the physical and chemical. It was found that current methods of analytical procedure gave little information concerning the bio-chemical property. Some study of dissolved oxygen in the Boston sewage indicated that there was an interesting relationship between temperature and dissolved oxygen, and it was assumed that this relation was of even deeper significance, and that the dissolved oxygen itself

¹ Tech. Quart. XXVIII, 1905, p. 40.

was an indirect measure of the condition of the sewage. With increasing temperature the dissolved oxygen normally present in sewage was found to decrease steadily until it completely disappeared. There was interesting graphical evidence that beyond this point there existed a condition of negative dissolved oxygen or oxygen avidity, a point which has since been experimentally demonstrated. Beyond this there was nothing in the methods of analysis in use at that time to indicate sewage condition. The older sewage chemistry, which was built about the nitrogen cycle, has proven itself utterly inadequate to meet the demands of modern studies in purification and in stream pollution. There has, therefore, in recent years, been a marked tendency toward a more detailed study of oxygen relationships with a corresponding elimination of much of the nitrogen work. This newer sewage chemistry has been developed along the line of putrescibility studies, although its scope has been extended far beyond that originally included under the term "putrescibility of sewage." The results have thrown further light upon the question of the condition of sewage as previously defined and have fully justified the emphasis which was originally given to this almost hypothetical characteristic.

In stream pollution studies it is the oxygen relations that are relied upon almost wholly. Modern sewage disposal and stream pollution questions have come to be less and less questions of sanitary significance, and more and more matters of physical nuisance; and the question of nuisance in a stream is now recognized to be merely a question of a balance between available oxygen and the oxygen demands of the polluting material. Under these circumstances determinations of free and albuminoid ammonia give no information whatever upon the real condition of the stream, nor could one, however experienced, deduce from an ordinary chemical analysis of sewage the effect of the discharge of a stated volume of such a sewage into a known body of water. In other words, no correlation has yet been discovered between the concentration and composition factors of sewage and its oxygen requirement. The latter is a purely bio-chemical property as is evidenced by the fact that a sterile sewage discharged into a sterile stream would have no

oxygen requirement, whatever might be its chemical analysis. The time is therefore opportune for a brief review of our present knowledge of the bio-chemistry of sewage as shown by its oxygen relationships.

The determination of dissolved oxygen in sewage and in effluents has always been an integral part of their chemical analysis. This determination was inherited along with the others from the older water analysis. No attempt at quantitative interpretation, however, was ever made, so far as the writer is aware, and the dissolved oxygen factor was recorded along with the nitrogen and other factors as a part of the general scheme of sewage analysis. It was assumed in general that the higher the dissolved oxygen and oxidized nitrogen the greater the purification. As long as purification was defined as oxidation of the nitrogenous constituents of the sewage and was made synonymous with nitrification, such an interpretation was unobjectionable. From the more modern viewpoint this conception of the rôle of oxygen is erroneous, as will be shown. Aside from the dissolved oxygen determination, no attention was given to the bio-chemical factors until the early efforts of the English chemists to measure putrescibility. A historical summary of these putrescibility studies has appeared in an earlier paper¹ and this matter will not be re-capitulated. It is sufficient to point out that in all these early attempts putrescibility was regarded as a definite property, the opposite of stability, and all measures of this property were qualitative. In the earliest form the test involved the storage of a sample of effluent in a tightly sealed bottle for a definite period of time. If it became foul-smelling it was reported as putrescible, if not, as stable. Later this test was placed upon a more definite basis by the discovery, in methylene blue, of a very satisfactory indicator. The use of this dye was first suggested by Spitta and later by Spitta and Weldert. In this country Phelps and Winslow² reported an extensive study of the method and urged its adoption in place of the indefinite smell test.

While the introduction of the methylene blue test was a dis-

¹ Phelps & Winslow, *Jour. Inf. Dis.*, Supp. #3, 1907, p. 1.

² Loc. cit.

tinct advance in putrescibility studies, the whole matter was still on a qualitative basis. The question whether an effluent was stable or not depended to a very large extent upon the technique of the test, particularly upon the establishment of a definite time and temperature. Obviously this procedure was fundamentally wrong. If stability be a definite qualitative characteristic it ought not to be possible to find an effluent stable by a four day test, and putrescible by a five day test, yet such a condition actually existed. If on the other hand, stability be looked upon as a quantitative property to be measured and stated in definite numerical terms, then all the analytical results are harmonized. This viewpoint is so fundamental to the present discussion that it will be illustrated more fully.

Putrescibility may be defined as the availability of the substance in question as a bacterial food. Stability is the converse of this. Protein material may be taken to represent one end of the scale and leaf mold or humus the other. Between these two extremes one may find organic substances of all degrees of availability as bacterial food. Sewage purification as we know it today, is a process of so altering the chemical properties of organic material as to increase its stability. This may or may not be accompanied by processes of nitrification. It is essentially oxidation. In its incomplete form it is principally oxidation of carbonaceous material and can be measured only on a stability scale. A high degree of purification may be obtained without any material oxidation of the nitrogen. This oxidation is commonly held to be biological. Upon this matter, however, there is some slight disagreement and very little real evidence. Whether it be primarily biological or primarily physico-chemical, but dependent upon a biological substratum matters little in practice. One might indeed urge that all life processes are essentially physico-chemical. Bio-chemical changes which take place during purification treatment have as their net result the shifting of the position of the organic matter towards the stable or humus end of the stability scale. Only in extreme cases is perfect stability reached. Therefore, any correct measure of sewage purification must be a quantitative one and a putresci-

bility or stability test must be devised to give quantitative results.

This problem has been approached from the standpoint of the mass action law of physical chemistry. A definite chemical reaction takes place during the storage of a sample of effluent in a tightly stoppered bottle. This reaction is a bio-chemical one maintained by the micro-organisms present. So far as reactions of this kind have been studied, they have been found to be monomolecular in a physico-chemical sense. As a first approximation it was assumed that this reaction also was of the first order. The final results justified this assumption. There is in this reaction then a gradual reduction of the available oxygen of the effluent and a corresponding reduction of the oxygen requirements of the organic matter present. These two reductions must balance. The velocity of the reaction follows the logarithmic curve of first order reactions. By the use of methylene blue as an indicator, the zero oxygen point is shown. If the oxygen available in the sample in the form of dissolved oxygen and of nitrates and nitrites were exactly equivalent to the maximum oxygen requirement of the organic matter, the reaction would proceed forever at a decreasing rate and the oxygen would never become exhausted. This is a condition which may be termed perfect stability in the effluent as a whole. This conception must be clearly distinguished, however, from stability in the organic matter alone. I have, therefore, called the former relative stability. It may be defined as the relation existing between the oxygen requirements of the organic matter present and the available oxygen existing in the effluent. Knowing the mathematical form of the reaction curve and the time required for the complete reduction of the available oxygen, it is a simple matter to compute in any case this relative stability term. This, then, is the true quantitative measure of the character of the effluent. An effluent having a complete relative stability has within itself the necessary oxygen reserve to complete its own oxidation. It will, therefore, abstract nothing from the stream. One having a 50 per cent relative stability has one half as much oxygen as it will eventually require. It will, therefore, abstract from the stream as much oxygen as it already

contains. In this way one can determine in advance the effect of the discharge of any particular kind of effluent into a given stream and can specify in definite quantitative terms the character of effluent which may be discharged into the stream without fear of nuisance.

This relative stability number as it has been worked out for various types of effluents is defined by the following formula:—

$$S = 100(1 - 0.794^t)$$

S is the relative stability number in per cent and t the time of decolorization at 20°. Temperature has an important effect upon all bio-chemical reactions and in this case it was found that the velocity was doubled between 20° and 37°; therefore, at 37° the formula becomes:—

$$S = 100(1 - 0.630^t)$$

This latter temperature may be used where quick results are required, but since in this case the bacteria at work are not those ordinarily working in the stream, the 20° temperature should be used in important investigations, or it should at least be employed to check the 37° results. If necessary a new 37° formula should be derived. Observations of the samples need not be made more frequently than every twelve hours, nor continued beyond four days in routine work. For very careful work a ten day period of observation will be necessary. In practice, however, it has been found sufficiently accurate to average all results over four days at 20° at a lump figure of 95 per cent.

From the 20 formula the following values are taken for convenience:—

| Reducing time t | Relative Stability S% | Reducing time t | Relative Stability S% |
|--------------------|--------------------------|--------------------|--------------------------|
| 0.5 | 11 | 8.0 | 84 |
| 1.0 | 21 | 9 | 87 |
| 1.5 | 30 | 10 | 90 |
| 2.0 | 37 | 11 | 92 |
| 2.5 | 44 | 12 | 94 |
| 3.0 | 50 | 13 | 95 |
| 4.0 | 60 | 14 | 96 |
| 5.0 | 68 | 16 | 97 |
| 6.0 | 75 | 18 | 98 |
| 7.0 | 80 | 20 | 99 |

The establishment of a quantitative basis for stability measurement was an important step but the matter was still in an incomplete stage. Relative stability in an effluent is capable of interpretation in terms of oxygen requirement but only indirectly. In a sewage devoid of oxygen there is no relative stability, yet sewages differ in putrescibility and the differences should be measurable.

Before proceeding with calculations of the effect of a given discharge of sewage upon a stream, two things must be known, the available oxygen of the stream and the oxygen requirements of the sewage.

The former is not always determinable but may generally be approximated. Our present discussion is concerned with the latter. This is the one fundamental value upon which the calculation must rest. It must not be relative to anything, but stated specifically, in milligrams per liter, the oxygen requirement.

In an effluent the result is obtained as follows:-

Relative stability, 75%

Oxygen available, free
and as N_2O_3 and N_2O_5 , 10 mg. p. lit.

Oxygen requirement, $0.25 \times 10 = 2.5$ mg. p. lit.

In a sewage two methods of treatment are available:-

A. The sewage is diluted in tap water in a suitable ratio, say 10% of sewage; the oxygen of the water being known. Methylene-blue is added as usual and the time of decolorization noted. This gives the relative stability of the mixture, from which its oxygen requirement can be obtained as above. The oxygen requirement of the whole sewage is ten times as great as this value.

Theoretically this gives the total oxygen requirement. Such is the nature of the reaction, however, that even in an excess of oxygen, only about half this requirement is utilized in four days. Under most conditions such a period of time suffices to carry the water to the sea or to a much larger stream with consequent greater dilution. The time element therefore must be considered. The rate of oxidation, or the total requirement in a specified time is necessary for a complete solution.

Here once more recourse is had to the known facts of physical chemistry. In a sufficiently dilute solution of sewage and aerated water, the oxygen withdrawn from the water during a specified period of time can be directly measured by determination of the oxygen present initially and after a definite time, say 24 hours. If the reaction be monomolecular with reference to the oxygen, as appears to be the case we have $\log(O - O_0) = KC^nt$.

When O is the initial and O_0 the final dissolved oxygen value, C the concentration of sewage, expressed in per cent by volume, t , the duration of the test in hours, and n , a concentration exponent, K is the velocity constant of the reaction to be determined. With K known the calculation may be reversed and with the initial oxygen of the stream, O , and the concentration in the stream, the final result, O_0 , may be determined at the expiration of any time. In dealing with effluents and with many sewages the exponent, n , was found to be unity and was omitted. Later work showed that this was not universally true and Lederer has since shown a considerable deviation in some cases. The value of n , however, is usually constant in any given case and may be determined by the proper study of a series of dilutions. If n be not constant in the particular case under consideration, then this formula is of less general nature and the concentration or dilution

in the test must be made to conform approximately with that in the stream. Under these conditions the effect after any stated period of time of the discharge of any volume of sewage into a stream of known volume and oxygen content is determinable.

This method of study has proven of great value in studies of New York Harbor and of the probable effect of partial purification; of concentration of the discharge at certain points; and of the addition of more sewage through the proposed Passaic Valley sewer.

Finally these methods permit for the first time the adoption of rational specifications for sewage effluents. This may be illustrated by an example. Let it be assumed that a certain body of water is the necessary final place of discharge for the sewage of a definite future population. A wise treatment of the problem by the state authority would involve the determination of the capacity of the body of water to receive sewage without danger of a nuisance. Questions of bacterial pollution are incidental and can be treated separately. The sewage may if necessary be disinfected without further treatment. Suspended matter, visible effects and deposits are also capable of separate treatment. With these matters settled there remains the question to what extent can the waters be utilized to carry on the work of purification. Let the oxygen capacity of the water be divided pro rata among the various populations, present and prospective, unless there be some strong economic reason for favoring one center of population, as there is in the case of lower New York City. Then each community may have for its own use its share of this oxygen. New works may be authorized with the specification that the effluent shall have a total oxygen requirement, in a definite number of days, not exceeding a definite value, expressed in pounds per day. This requirement is determined by the method outlined, the value found in milligrams per liter being multiplied by the total discharge in liters per day and converted into pounds. The sum of all these amounts must not exceed the capacity of the water, and small growing communities will not at once be burdened with expensive works. Neither will any community be put to an unfair expense for excessive and disproportionate purification as so often happens at present.

It would be the duty of the state authority to warn the community from time to time of the state of its oxygen appropriation, and to estimate at what date partial purification should be begun. In this way towns and cities will be permitted to take advantage of the rapid improvements in the art of sewage disposal and incentive will be given to further studies in cheap, partial purification methods, which at the present day are so essential to the successful solution of the sewage disposal problems in large cities.

In this day of conservation and efficiency it remains for the investigator in the underlying bio-chemical principles of sewage purification to point out a safe middle course between the autocratic and often unduly severe requirements of state authority on the one hand, and, on the other, the almost criminal destruction of the invaluable natural resources of our waters.

SUGGESTED INTERNATIONAL TEST FOR DISINFECTANTS

S. RIDEAL
London, England

The standardization of disinfectants has lately been the subject of considerable discussion in America, and among a number of authors of recent papers dealing with the theory of disinfection may be mentioned Phelps, Anderson, Dreyfus, S. & E. K. Rideal, while practical methods have been discussed by Kendall, Edwards, Anderson and McClintic. The two latter are authors of the Hygienic Laboratory coefficient method for determining the germicidal value of disinfectants, which has been adopted to some extent in the United States.

The H.L.P.C. test is mainly based on modifications of the Rideal-Walker method suggested by the *Lancet* Commission. The final results is the mean of two coefficients obtained at $2\frac{1}{2}$ and at 15 minutes, and in order to hit off the two points with both disinfectant and control carbolic in the one chart, a large number of dilutions of the disinfectant and of carbolic acid have to be employed, resulting in as many as 76 sub-cultures during the 15 minutes. This entails the use of 4 to 6 platinum loops and special sterilising apparatus. This test has been discussed by S. Rideal, who points out the necessity for the universal adoption of one standard method for disinfectant testing. The chief criticisms made are that the H.L.P.C. method would be too expensive and cumbersome for everyday control work and that the same results may be arrived at by a simpler test. The scheme for a universal test incorporating the more important modifications of the original R. W. test is briefly outlined as follows:—

- (1) Organism—*B. typhosus*.
- (2) Test Culture—Sub-cultured and filtered (as recommended by Anderson & McClintic)

(3) Temperature of disinfection— 20°C (as recommended by Anderson & McClintic)

(4) Dose of test culture to disinfectant 0.1 c.c. per 5 c.c. measured from a graduated pipette (as recommended by Anderson & McClintic)

(5) Calculation of results—from an empirical time (yet to be fixed) with the 15 duration of the test. (as recommended by Chick and Martin)

This test is practically the same as the H.L.P.C. method except that such extensive test charts would not be required. Calculating on the basis of $7\frac{1}{2}$ minutes as the fixed time for sterility, from the H.L.P.C. test charts of over 50 different disinfectant preparations examined by McClintic, it was found that the results agreed very closely with the reported H.L.P.C. values, the greatest divergence being only 0.48 in the case of a coefficient of over 12.

(*Abstract*)

THE WATER-SUPPLY OF FARM HOMESTEADS IN CANADA

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The object of this paper, primarily, is to call the attention of those who are working for the advance of agriculture to the condition of the water as used on the average farm, in the hope that by concerted action an improvement in its quality may be effected. There is great need of a campaign throughout the country generally for better water, better ventilation in the houses, better cooking, etc., and much good might be accomplished by those entrusted with agricultural education at our Colleges and Experiment Stations by analysis, demonstration and the dissemination of information relating to these matters.

Secondly, it gives an account of the work carried on by the Chemical Division of the Dominion Experimental Farms since their establishment (1887) in the examination of water supplies of farmers, cheese factories and creameries in Canada. During these twenty-five years several thousands of these waters have been examined, with a result that judged by accepted standards, probably not more than one third of them are pure and wholesome.

The source of the supply, both for man and beast, on the majority of farms is the shallow well that merely collects "ground water," the soakage from the surrounding soil. Too often convenience alone is consulted in locating the well and as a consequence we find it in the barnyard or dangerously near the privy or other source of contamination. After a few years, even on new homesteads, the water finding its way into such wells will be seriously polluted. These waters are no doubt the cause in many instances of ill health on the farm and at times we have

been able to show that they are directly responsible for an outbreak of typhoid fever. Precautionary methods for the protection of such wells are outlined but the ground is taken that they should be abandoned. Driven or bored wells, tapping a deep-seated source and from which soakage and surface wash are carefully excluded, are advocated. These as a rule yield water free from organic pollution.

The various classes of natural waters used by farmers are briefly discussed and especial mention is made of the remarkable purity of the water of the glacier stream as occurring in British Columbia and Alberta. The character of "slough" water and of waters from wells sunk in areas of scanty rainfall is considered and the nature of their saline content outlined. In many instances distillation must be resorted to in order to obtain from these "alkali" waters a potable supply. The normal waters of the lakes, streams and springs in which Canada abounds are with very few exceptions eminently suited for domestic use; over the larger proportion of the Dominion's area there are no insuperable difficulties in obtaining an ample and pure supply.

The paper has been written from the sanitary rather than the chemical standpoint, but observations have been made as to the extent that "standards" and "limits" can be used in diagnosis.

NEW FORM OF APPARATUS FOR THE DETERMINA- TION OF DISSOLVED OXYGEN IN WATER

GEORGE A. SOPER

New York, N. Y.

This apparatus consists of a bottle, usually of about 500 c.c. capacity, with a long funnel-shaped lip. A stopper which is convex at the bottom fits accurately into the neck and when in place permits about 15 c.c. of liquid to stand in the funnel without overflowing. The capacity of the bottle is accurately determined with the bottle in place.

In use the bottle is filled to the beginning of the funnel with the water to be examined and the stopper is set down in place. The excess of water which rises in the funnel is poured off. The stopper is removed and to the bottle of about 500 c.c. capacity, 6 c.c. of a standard solution of ferrous sulphate¹ are delivered by a pipette to the bottom of the bottle where it remains unless the bottle is agitated. The stopper is replaced and the water which rises in the funnel is poured off. Five c.c. of sodium carbonate solution (200 grams per litre of water) are then poured into the funnel. The stopper is cautiously raised sufficiently to allow the heavy alkali to sink through the water to the bottom of the bottle, where the reaction producing a heavy precipitate begins. The stopper is set back in place, the water in the funnel is poured off and the bottle is shaken until the free oxygen is entirely absorbed. Ten c.c. of a 50 per cent. solution of sulphuric acid is poured into the funnel and the stopper raised sufficiently to permit the heavy acid to diffuse, discoloring and permitting the contents of the bottle to be titrated. Finally, the contents are poured into an Erlenmeyer flask and titrated with permanganate of potash, each c.c. of which represents 1 c.c. of oxygen.

¹ 144 grams crystallized ferrous sulphate are dissolved in water, 15 c.c. concentrated sulphuric acid are added and the whole made up to 3 litres.

A blank determination is made whenever the water contains much organic matter or sodium chloride. The same steps are followed in making the blank as in making the analysis except that the sodium carbonate is omitted. The difference between the permanganate required by the blank and that absorbed in the actual analysis represents the dissolved oxygen present.

The purpose of this apparatus which was devised by the author is to permit of the addition of reagents to the bottle without exposing the contents of the bottle to the air.

The reagents used are as follows:

Standard Ferrous Sulphate. This is prepared by dissolving 144 grams of Kahlbaum's crystallized ferrous sulphate in water, adding 15 cubic centimeters of concentrated sulphuric acid and diluting the whole to 3 litres.

Standard Sodium Carbonate. Prepared by dissolving 200 grams of sodium carbonate crystals in 1 litre of water.

Standard Sulphuric Acid. Prepared by mixing equal parts of concentrated sulphuric acid and water.

Standard Potassium Permanganate. Prepared by dissolving 25.4 grams of potassium permanganate in water and diluting to 4.5 litres. This reagent is to be standardized against especially prepared Mohr's salt.

A PRACTICAL FIELD METHOD FOR THE DETERMINATION OF DISSOLVED OXYGEN IN WATER

GEROGE A. SOPER AND PAYN B. PARSONS

New York, N. Y.

The method here described has been used by the authors in over 5,000 tests of land and sea water and mixtures of the two, chiefly in the vicinity of New York harbor. It is well suited for use in the field, as well as in the laboratory, a large part of the work having been performed on boats sometimes in a rough sea and in stormy weather. It has been repeatedly tested beside the Winkler and boiling out methods and is believed to be more accurate than either, especially in the presence of nitrites in large amount.

The fundamental principle of the test is the absorption of the dissolved oxygen by ferrous sulphate and the subsequent titration of the unconsumed ferrous sulphate by permanganate of potash. This procedure with other modifications has been extensively used, especially in Europe, but heretofore only with non-saline waters. Originality is claimed for the adaptation of the technique to field use and to tidal waters. One of the authors is chiefly responsible for the details of technique, while the practical work of the large number of tests has been performed by the other. It is suggested that the method be known as the Soper-Parsons modification of the ferrous sulphate method. The details follow:

Water for analysis is preferably collected in a separatory funnel of about 350 cubic centimeters capacity. The funnel is connected with an empty bottle of much larger capacity. Both fit securely in a heavy case. The bottle has a rubber stopper perforated for two grass tubes, one of which extends 1 inch below the stopper and 2 inches above, while the other extends to the bottom of the bottle and is connected at the top by means of heavy rubber tubing with the separatory funnel. The top of the

separatory funnel emerges through a small opening in the cover of the case. The rubber stopper of the funnel is perforated by two glass tubes, one of which extends to the bottom of the funnel and 1 inch above the stopper and the other to the bottom of the stopper and connected above to the bottle by heavy rubber tubing.

The apparatus is rapidly lowered to the required depth by means of a one-half inch manila rope marked off in feet. The open end of the tube in the separatory funnel being lower than that of the large bottle, the water enters through the long tube of the separatory funnel and flows through the funnel into the bottle, so that when the bottle is full, as indicated by the cessation of air bubbles rising to the surface of the water, the separatory funnel has been filled and emptied several times.

After being filled with the sample to be analyzed, the separatory funnel is removed from its case and 6 c.c. of ferrous sulphate and 4 c.c. of sodium carbonate are added, both being delivered by a pipette near the bottom of the funnel. The stopper is then replaced and the contents are shaken. The dissolved oxygen in the presence of the alkali immediately acts upon a portion of the dissolved salt, precipitating it. After 5 minutes the funnel is inverted and 10 c.c. of standard sulphuric acid are introduced through the stem of the funnel, the stop-cock being opened for this purpose. After the acid has mixed thoroughly with the other contents, the funnel is allowed to stand until the mixture is sufficiently colorless and clear, usually about 5 minutes. The contents of the funnel are then emptied into an Erlenmeyer flask and titrated with standard potassium permanganate.

A blank sample, which has been collected in a similar manner to the first, is now examined. In this case the separatory funnel is filled, as in the previous test, 10 c.c. of the standard sulphuric acid are added and the whole shaken. Then 6 c.c. of standard ferrous sulphate are added and the funnel again shaken. The mixture is then run out into an Erlenmeyer flask and titrated with standard potassium permanganate. In this case the acid reaction prevents the dissolved oxygen from acting upon any of the ferrous salt.

By subtracting the result of titrating the first sample from

the result of titrating the second, the amount of ferrous salt acted upon by the dissolved oxygen in the water is obtained. The results are stated in terms of cubic centimeters of dissolved oxygen per litre of water.

Suppose 1 c.c. of permanganate equals 1.009 c.c. of oxygen at 0 degrees Centrigrade and 760 millimeters pressure. The difference between the two titrations is multiplied by 1.009 and by 1,000 and divided by the number of cubic centimeters of water contained in the funnel.

It is sometimes convenient to express the amount of dissolved oxygen found in terms of percentage of its saturation value. The percentage of saturation of each sample can be calculated from a diagram prepared from a table contained in the Fifth Report of the Royal Commission on Sewage Disposal of Great Britain, Appendix VI, which gives the saturation figures at different temperatures for sea water and distilled water.

The form of separatory funnel employed is substantially the same as recommended by Prof. E. A. Letts and described in the same reference.

The reagents required are as follows:

Standard Ferrous Sulphate. This is prepared by dissolving 144 grams of Kahlbaum's crystallized ferrous sulphate in water, adding 15 cubic centimeters of concentrated sulphuric acid and diluting the whole to 3 litres.

Standard Sodium Carbonate. Prepared by dissolving 100 grams of sodium carbonate crystals in 1 litre of water.

Standard Sulphuric Acid. Prepared by mixing equal parts of concentrated sulphuric acid and water.

Standard Potassium Permanganate. Prepared by dissolving 25.4 grams of potassium permanganate in water and diluting to 4.5 litres. This reagent is to be standardized against especially prepared Mohr's salt.

SANITARY PROTECTION OF THE WATER SUPPLIES TAKEN FROM THE GREAT LAKES

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More than five million people live in cities and towns near the shores of our Great Lakes. Most of these communities take their water supplies from the lakes and discharge their sewage into them. Except where the water supply has been purified before being used this practice has very seriously affected the health of the lake cities and has been the cause of much loss of life. With our present sanitary knowledge it seems strange that such a filthy practice should have ever been tolerated. It is still more strange that raw lake water should continue to be used in cities which are doing so much in other ways to improve public hygienic conditions. The object of this paper is to set forth the problem in its various aspects, to show the effect of the use of raw contaminated lake water on the public health and to point out the ways in which the problem has been solved or may be solved under different local conditions.

THE GREAT LAKES

The Great Lakes drain an area of nearly three hundred thousand square miles, of which about two-thirds is land area and one-third water area. The figures in the accompanying table show the relative magnitude of the various lakes.

Lake Superior is the largest body of fresh water on the globe. According to the U. S. Lake Survey (Bulletin 14) "it is characterized by deep water, and high and rocky shores along a large portion of its coast. Compared with the other Great Lakes, its surface is more elevated above the sea; it is more irregular in outline, has deeper and colder water, more fog and ice, but less rain; the winds and seas are not greatly different from those of

Data Relating to the Great Lakes

| Lake | Square Miles | | | Mean elevation above sea level at New York | Maximum observed depth feet |
|----------------|--------------|---------------|---------|--|-----------------------------|
| | Land surface | Water surface | Total | | |
| Superior..... | 48,600 | 31,800 | 80,400 | 602.28 | 1,012 |
| Michigan..... | 45,700 | 22,400 | 68,100 | 581.36 | 864 |
| Huron..... | 52,100 | 23,200 | 75,300 | 581.41 | 750 |
| St. Clair..... | 6,335 | 495 | 6,780 | | |
| Erie..... | 24,480 | 9,932 | 34,412 | 572.62 | 210 |
| Ontario..... | 25,720 | 7,260 | 32,980 | 246.2 | 738 |
| Total..... | 202,935 | 95,037 | 297,972 | | |

the other lakes." The major axis of the lake lies east and west. The lake discharges at its east end through the St. Mary's river into Lake Huron. The discharge at mean stage was measured in 1902 and found to be 60,600 c. f. s. Lake Superior has few large cities on its shores and for the most part these are widely separated. Lake Superior has a shore line of about 1,925 miles, of which about 925 miles are in Canada. Of the remainder about 185 miles are in Minnesota, 185 miles in Wisconsin and 630 miles in Michigan.

The major axis of Lake Michigan lies north and south, except that in the northern part it turns easterly. Its average depth is about 288 feet and its capacity 179 million cubic feet. Its elevation is about the same as that of Lake Huron with which it connects through the Straits of Mackinac. Its natural discharge is about 87,000 c. f. s. Lake Michigan also has an artificial outlet through the Chicago River, the Drainage Canal, the Des Plaines River and the Illinois River westward into the Mississippi River, through which the flow is between 6,000 and 7,000 c. f. s. at the present time. The east shore of Lake Michigan is sandy and the harbors are not good. On the western shore there

are a number of better harbors, located usually at the mouth of some river. These rivers are for the most part small. Green Bay is an important arm of the lake on the west side. The pollution problem at the southerly end of Lake Michigan is a more important one than elsewhere in the Great Lakes, as there are numerous cities along the shore relatively near together. Lake Michigan has no Canadian boundary. Its shore line in the United States is about 1,470 miles, 905 miles of which are in Michigan, 450 miles in Wisconsin, 60 miles in Illinois and 55 miles in Indiana.

Lake Huron lies northwest and southeast. It discharges into Lake St. Clair through the St. Clair River, the discharge at mean stage being about 212,000 c. f. s. Georgian Bay is an important arm of the lake on the east side. Lake Huron is relatively unimportant from a water supply standpoint, as there are few large cities along its shores. It has about 1,900 miles of shore line, of which 1,320 miles are in Canada and 580 miles in the State of Michigan.

Lake St. Clair is a relatively small body of water through which a 20-foot channel has been dredged. It discharges into the Detroit River, which in turn flows into Lake Erie. It has only about 155 miles of shore line and no large cities are situated upon it.

Lake Erie is the shallowest of the Great Lakes. Its average depth is only 63 feet and its maximum depth 210 feet. Its capacity is about 17,500,000 cubic feet. Its axis lies east-north-east and west-southwest. Ordinarily calm, it is easily influenced by the high winds, which raise dangerous seas. Lake Erie discharges through the Niagara River into Lake Ontario. The discharge over Niagara Falls at mean stage is said to be about 227,300 c. f. s. There are a number of relatively large cities along the southern shore of Lake Erie, but most of these are widely separated. The shore line of Lake Erie is about 820 miles long. Of this about 340 miles are in Canada, 45 miles in Michigan, 290 miles in Ohio, 65 miles in Pennsylvania and 80 miles in New York State.

Lake Ontario, the last and smallest of the chain of Great Lakes, except Lake St. Clair, lies nearly east and west. It is

comparatively deep and accordingly the fluctuations of level are relatively less than on Lake Erie. It discharges into the St. Lawrence River, the discharge at mean stage being about 270,000 c. f. s. The capacity of the lake is about 450 million gallons. There are relatively few large cities located on Lake Ontario, the most important one being Toronto, Ont. The total shore line of Lake Ontario is about 980 miles, of which 600 miles are in Canada and 380 miles in New York State.

QUALITY OF THE BROAD WATERS OF THE GREAT LAKES

Generally speaking the water of the Great Lakes away from the shores is of excellent quality for the purposes of a public water supply. It is rather hard, but is softer than most of the water supplies taken from streams or from the ground in the same general catchment area. Lake Superior water is somewhat softer than that of the other lakes. This is shown by the figures given on page 275, taken from a report by R. B. Dole on the Quality of Surface Waters in the United States (U. S. G. S. Water Supply Paper No. 236).

The total hardness of Lake Superior water was 45, Lake Michigan water 99, Lake Huron water 89, Lake Erie water 108, and the St. Lawrence River water 107 parts per million. The permanent hardness likewise increased from about 3 parts per million in Lake Superior to 13.5 parts per million in Lake Erie. These figures correspond well with other data published elsewhere in connection with the water supplies of particular cities.

The chlorine is slightly higher in Lake Michigan and Lake Huron than in Lake Superior. It increases considerably in Lake Erie on account of the effect of the salt water from the oil well region of Ohio, which enters Lake Erie at the westerly end at various points between Toledo and Sandusky. In some parts of the lakes in the vicinity of these cities the chlorine in the water exceeds 10 parts per million; opposite Cleveland it ranges from 6 to 8 parts per million and at Buffalo it averages about 7 parts per million; in Lake Ontario it decreases slightly, presumably because of dilution.

The lake waters contain less than 0.1 part per million of iron.

ANALYSES OF GREAT LAKE WATERS

| | Lake Superior at Sault Ste. Marie | Lake Michigan at St. Ignace | Lake Huron at Port Huron | Lake Erie at Buffalo | St. Lawrence River at Ogdensburg |
|---|---|--------------------------------|-----------------------------|-------------------------|--|
| Parts per Million | | | | | |
| Total dissolved solids... | 6.0 | 118.0 | 108.0 | 133.0 | 134.0 |
| Turbidity..... | 2 | tr. | tr. | 41.0 | 4.5 |
| Silica (SiO_2)..... | 7.4 | 10.0 | 12.0 | 5.9 | 6.6 |
| Iron (Fe)..... | .06 | .04 | .04 | .07 | .05 |
| Calcium (Ca)..... | 13.0 | 26.0 | 24.0 | 31.0 | 31.0 |
| Magnesium (Mg)..... | 3.1 | 8.2 | 7.0 | 7.6 | 7.2 |
| Sodium & Potassium (Na & K)..... | 3.2 | 4.7 | 4.4 | 6.5 | 6.3 |
| Carbonate radicle (CO_3)..... | 0.0 | 2.9 | 1.8 | 3.1 | 2.9 |
| Bicarbonate radicle (HCO_3)..... | 56. | 112.0 | 100.0 | 114.0 | 116.0 |
| Sulphate radicle (SO_4)..... | 2.1 | 7.2 | 6.2 | 13.0 | 12.0 |
| Nitrate radicle (NO_3)..... | 0.5 | 0.8 | 0.4 | 0.3 | 0.3 |
| Chlorine..... | 1.1 | 2.7 | 2.6 | 8.7 | 7.7 |
| Per cent of Dry Residue | | | | | |
| Silica (SiO_2) | 12.7 | 8.5 | 11.11 | 4.5 | 5.0 |
| Iron oxide (Fe_2O_3) | 0.2 | 0.0 | 0.0 | 0.1 | 0.1 |
| Calcium (Ca) | 22.4 | 22.2 | 22.3 | 23.4 | 23.6 |
| Magnesium (Mg) | 5.3 | 7.0 | 6.5 | 5.7 | 5.5 |
| Sodium & Potassium (Na & K) | 5.5 | 4.0 | 4.1 | 4.7 | 4.8 |
| Carbonate radicle (CO_3) | 47.5 | 49.6 | 47.4 | 44.8 | 45.7 |
| Sulphate radicle (SO_4) | 3.6 | 6.1 | 5.8 | 9.8 | 9.2 |
| Nitrate radicle (NO_3) | 0.9 | 0.3 | 0.4 | 0.2 | 0.2 |
| Chlorine (Cl) | 1.9 | 2.8 | 2.4 | 6.6 | 5.9 |
| Parts per Million | | | | | |
| Total Hardness (Calculated from Ca and Mg) | 45.4 | 99.2 | 89.2 | 108.2 | 107.5 |
| Permanent hardness (calculated from SO_4 radicle only) | 2.2 | 7.5 | 6.5 | 13.5 | 12.5 |

The amount of organic matter in the broad waters of the lakes is very small. The waters have a very low color, usually less than 10, and are practically tasteless and odorless. Occasionally slight growths of algae occur, but they are almost never troublesome, except when the water is stored in open reservoirs before use.

The numbers of bacteria in the broad waters of the lake are almost invariably small. The bacterial counts made on gelatine at 20° C according to standard methods are normally less than 100 per cc. during the greater part of the year. In summer they are less than this. After periods of rain and high winds they increase somewhat.

Of the condition of the water at the bottom of the lakes where deepest, its temperature, its dissolved gases, etc., very little is known.

Quality of the Shore Water

The water near the shores of the lake may be quite different in quality from that farther out. This depends much upon the character of the shore, the proximity and character of inflowing streams, the season of the year, the wind, and many minor factors. Generally speaking, the shore water is more turbid and contains larger numbers of microscopic organisms and bacteria than the broad waters of the lake, and what is more important, it is more likely to be contaminated with sewage discharged either directly into the lakes or into streams that flow into them. In the vicinity of large cities, and especially when these are situated upon large rivers, the pollution of the shore waters is a very serious matter.

The turbidity of the shore water is caused in part by washings from the land and in part by disturbances of mud deposits that have already taken place in the lake. During the author's investigation of the water of Lake Erie in the vicinity of Cleveland, in 1904, samples of water were collected at various distances from the shore near the city where the lake was polluted and at some distance from the city where the pollution was relatively small. Weekly analyses made between June 8th and August 26th showed the following average turbidities at different distances from the shore, at a point four miles west of the city, where the lake was but little contaminated.

Owing to the varying amounts of suspended matter carried the shore water commonly differs in appearance at different distances from the shore. The apparent color of the water varies from a dull brown to a deep blue. Not infrequently there is a series of well-defined color zones. This was strikingly illustrated at Cleveland on March 15th, 1904, when an extended series of observations was made. It was found that at that time there were four distinct zones of water of different color and these zones were defined with great sharpness. Near the shore and extending out to a distance of about 1.5 miles to a depth

**QUALITY OF LAKE ERIE WATER AT DIFFERENT DISTANCES
FROM THE SHORE NEAR CLEVELAND**

| Distance from the shore in miles | Depth in feet | Chlorine parts per million | Turbidity | Color | Number of bacteria per cc. |
|----------------------------------|---------------|----------------------------|-----------|-------|----------------------------|
| 1 | 40 | 6.5 | 23 | 11 | 731 |
| 2 | 44 | 6.3 | 17 | 8 | 957 |
| 3 | 48 | 6.1 | 11 | 9 | 661 |
| 4 | 54 | 6.1 | 10 | 7 | 378 |
| 6 | 57 | 6.2 | 8 | 5 | 465 |
| 8 | 60 | 6.1 | 7 | 5 | 219 |
| 10 | 66 | 6.1 | 3 | 3 | 197 |

of 35 feet, the water had a dark brown color. Outside of this there was a zone one mile wide where the water was of a light brown color. Beyond this was a zone two miles wide where the color was Nile green and still further beyond was the deep blue water of the lake. The turbidity of the water and the number of bacteria present in the different zones are shown by the following table:

**QUALITY OF SHORE WATER AT CLEVELAND, OHIO,
MARCH 15, 1904**

| Zone of | Distance from shore in miles | Depth in feet | Turbidity | Bacteria per cc. |
|------------------|------------------------------|---------------|-----------|------------------|
| Dark Brown water | 0 to 1.5 | 0 to 35 | 25 | 2500 or more |
| Brown water | 1.5 to 2.5 | 35 to 45 | 15 to 25 | 1250 to 2500 |
| Green water | 2.5 to 4.5 | 45 to 55 | 5 to 15 | 100 to 2250 |
| Blue water | 4.5 to 6.5 | 55 to 65 | 5 or less | 100 or less |

It will be noticed that the turbidity varied from more than 25 in the dark brown water near the shore to less than 5 in the blue water, and that the bacteria decreased from more than 2,500 per cc. in the dark brown water to less than 100 per cc. in the clear blue water of the lake.

Similar variations in the turbidity and number of bacteria at different distances from the shore have been observed by others, and especially by those who have studied the condition of the lake water at the southerly end of Lake Michigan. For example, Barnard and Brewster in their study of the sanitary condition of the southern end of Lake Michigan, bordering Lake County, Indiana, between August 19th and September 27th, 1908, found the following numbers of bacteria present at different distances from the shore.

| Distance from the shore in miles | Average number of bacteria per cc. |
|-------------------------------------|---------------------------------------|
| 0 to 1 mile | 174,000 |
| 1 mile | 15,000 |
| 2 miles | 6,600 |
| 3 " | 5,800 |
| 4 " | 4,400 |
| 5 " | 1,000 |
| 6 " | 200 |

At Milwaukee the width of the zone of turbid shore water varies in different places, according to the profile of the bottom of the lake.

Generally speaking the wind does not stir the bottom deposits to any appreciable extent where the water is more than about 40 feet deep. Only with extraordinary wind velocities are the deposits disturbed at great depths. Undertow currents may carry turbid water out to considerable distances from the shore, and thus give a false impression of disturbances at greater depths. The effect of the shore wash and the disturbance of bottom deposits, taken in connection with the undertow currents, however, is so great that no water supply intake has yet been carried far enough from the shore to avoid the occasional drawing of turbid water.

One of the longest water supply intakes is that of Cleveland, which is four miles from the shore in 50 feet of water. Between February 15, 1904, and June 30, 1905, the following turbidity observations were recorded of water at the pumping station:

Turbidity of Lake Erie Water at Cleveland, Ohio

| Month | | Minimum | Maximum | Average |
|------------|------|---------|---------|-----------------|
| February, | 1904 | 10 | 20 | 15 ¹ |
| March, | " | 3 | 18 | 10 |
| April, | " | 4 | 100 | 35 |
| May, | " | 10 | 45 | 23 |
| June, | " | 5 | 75 | 31 |
| July, | " | 0 | 15 | 3 |
| August, | " | 0 | 20 | 3 |
| September, | " | 5 | 5 | 5 ² |
| October, | " | 5 | 30 | 9 |
| November, | " | 5 | 90 | 28 |
| December, | " | 10 | 100 | 40 |
| January, | 1905 | 5 | 90 | 22 |
| February, | " | 4 | 5 | 4 |
| March, | " | 3 | 30 | 5 |
| April, | " | 4 | 50 | 8 |
| May, | " | 4 | 20 | 5 |
| June, | " | 0 | 7 | 2 |

Effect of Inflowing Streams on the Quality of Lake Waters

Many of the large cities of the lake are located at the mouths of rivers. This fact has an important bearing upon the quality of the local water supplies, for the streams are usually polluted with sewage and when the rivers are in flood their waters may be traced for a considerable distance into the lake. Not that these streams preserve their integrity through the lake waters, but rather that the river waters mix with and become diluted by the water of the lake, so that the latter become polluted over a fan-shaped area which varies in distance and spread according to the volume of the river and the wind currents in the lake. At times the effect of the river waters can be detected by the senses for several miles off shore. Thus at Cleveland the water of Lake Erie at the old intake, 1.5 miles from the shore,

¹ Three observations only.

² Four " "

frequently had an oily odor, while with a strong off-shore wind the oily odor could be sometimes detected even further out. It is said that at times it has been detected even at the new intake four miles from the shore. At the east of Lake Ontario at certain seasons the dark brown water of the Black River can be followed into the lake by its color for a number of miles.

Movements of the Water

Before discussing the question of lake pollution it is important to consider the movements of the water in the lakes for upon them depends the manner in which the inflowing sewage is mixed with the water and dispersed. They may be discussed under the following heads: (1) Movements of Translation. (2) Drift Currents. (3) Seiches. (4) Vertical Currents (Temperature currents). (5) Local Wind Currents. (6) Undertow Currents.

Movements of Translation

The waters of the lakes do not move as slowly flowing rivers towards their outlets, as these movements of translation are masked by the more active currents due to other causes. There is, of course, an outward flow but the actual velocity of the water from this is extremely small.

Thus the cross-section of Lake Erie at Cleveland is about 20 million square feet and the quantity of water passing about 200,000 cubic feet per second, hence the theoretical easterly movement of translation is 36 feet per hour, or 0.16 mile per day. The capacity of Lake Erie is about 17,000,000 cubic feet, the discharge at Niagara Falls about 227,000 cubic feet per second; hence the storage in the lake represents the flow for about two and a half years.

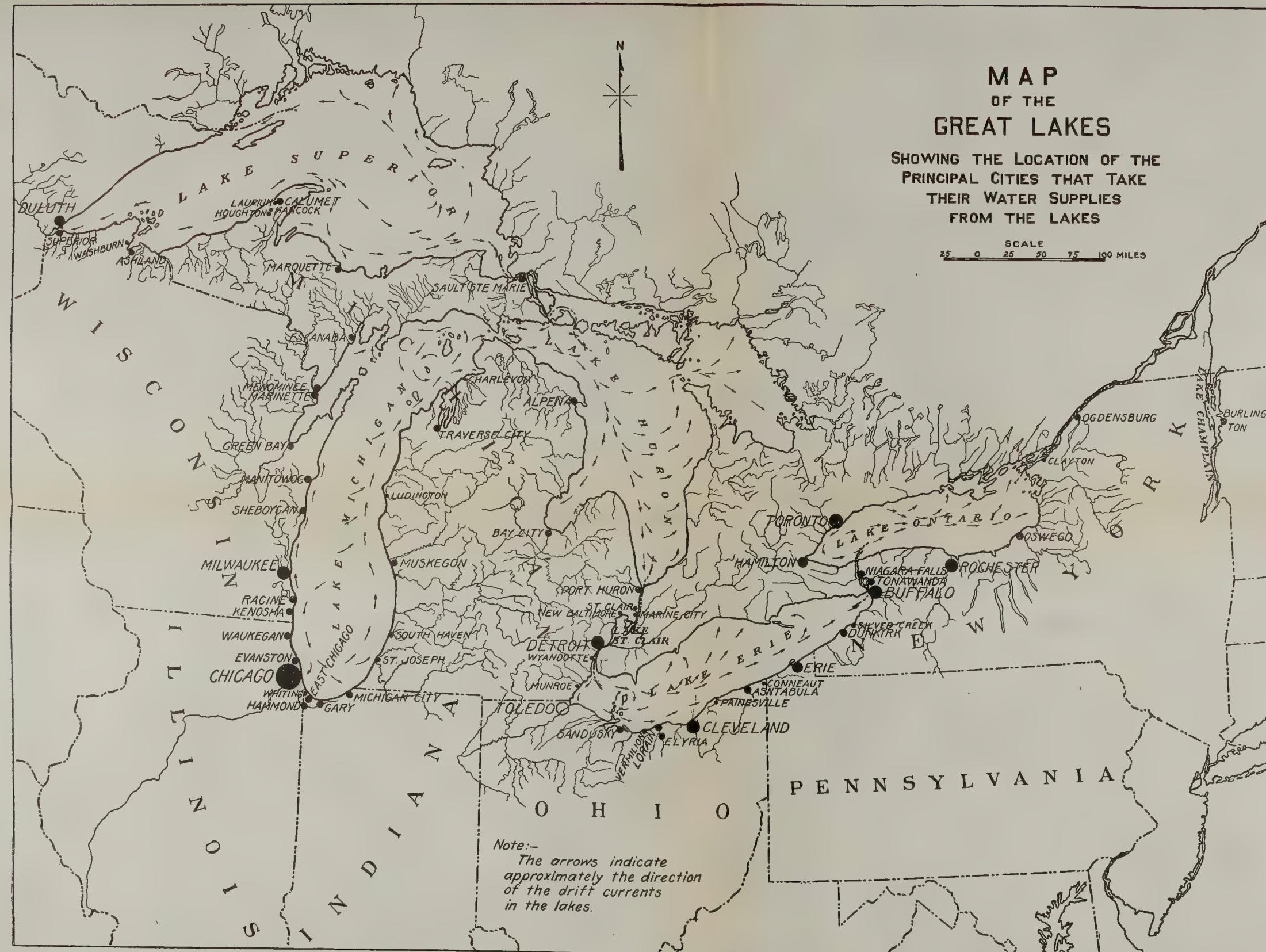
In Lake Ontario the period of storage is still longer for the cubical capacity of the lake is 60,000,000 cubic feet, and the discharge 270,000 cubic feet per second. The lake thus holds as much water as flows through it in 7.3 years. Kuichling has calculated that opposite Rochester the discharge is 237,000 c.f.s. and the easterly movement of translation, 193 feet per day.

In Lake Michigan the storage is equal to the natural discharge in a hundred years, and in Lake Superior it is still greater.

MAP OF THE GREAT LAKES

SHOWING THE LOCATION OF THE
PRINCIPAL CITIES THAT TAKE
THEIR WATER SUPPLIES
FROM THE LAKES

SCALE
25 0 25 50 75 100 MILES



Drift Currents

In all of the lakes there are drift currents of the broad waters near the surface due to the resultant action of the prevailing winds. Near the shore these currents are modified by the contours of the shore and reflected currents or eddies are formed. There are also return currents or deep drift currents induced by the general drift of the water towards a shore. These drift currents have been somewhat carefully studied by the U. S. Weather Bureau and maps have been prepared on which the surface currents are shown by arrows which represent the results of observations of the paths of many floats.

At the southerly end of Lake Michigan there is a southerly drift of the water on the west side past Milwaukee and Chicago, and a northerly drift of the water on the east side. The reason for this is that the prevailing wind at Chicago is from the southwest (S 53°W) and at Grand Haven, on the east shore opposite Milwaukee, is more nearly towards the north (S 39°W). The surface water being thus driven easterly and northerly at the south end of the lake, causes an induced southerly drift at Milwaukee, where also the prevailing winds are northerly rather than southerly (N 87°W). The wind records at Milwaukee from 1900 to 1909 show that the winds blowing southerly exceed those blowing northerly by about 3,000 miles per year. This unbalanced wind movement sets up a southerly drift of the surface water. This results in a drift of perhaps half a mile a day, or 150 miles a year, if the travel of the surface water is taken, as it commonly is, as 5% of the wind movement. This drift would not be constant, for the wind at Milwaukee seldom blows without change from the north for a week at a time, and although the wind movement to the south is 3,200 miles a year more than that toward the north, the latter amounts to 25,600 miles per year and the former to 28,800 miles.

At Cleveland there is a large excess of wind movement from the west; that is, down the lake, which amounts to about 24,490 miles per year, or an average of 67 miles per day. This excess occurs eleven months in the year, being greatest during the winter. If the surface water travels at the rate of 5% of that of

the wind the average surface drift would be 3.35 miles per day, and the maximum in the winter, 7.5 miles per day. The drift currents are naturally less near the shore than in the broad waters of the lake. When they impinge on jutting points they are deflected—sometimes towards the shore forming eddies when there are well-defined bays, as for example, in Lake Erie near Lorain and Sandusky. These eddy currents have been studied only to a limited extent.

These general drifts of the surface waters are well known by navigators and fishermen, and advantage is taken of them in locating water works intakes and sewer outfalls, so that the sewage will be carried away rather than towards the intake. This practice is good as far as it goes, but confidence in it has been in the past altogether too great and wholly unwarranted by the facts as they are now known. Two great factors have been left out of account,—the drift currents are not constant, and the intakes are located at some distance below the surface and well within the range of the undertow currents.

When the winds drive the water to the end of a lake, the level of the lake is raised and the increased head causes a return current near the bottom or beneath the neutral axis. Relatively little is known of these deep return currents beyond fragmentary bits of evidence obtained by experience. For example, near the shore of Lake Ontario overturned boats with the spread sails acting as submerged boats have been carried westward against a strong wind blowing towards the east. Dead bodies have been carried westward against a general easterly drift of the surface water. Fishermen's nets at the bottom of Lake Erie have been found clogged with debris on the lower side. That such deep return drift currents exist, however, is a natural inference from studies of the undertow that have been made at various places.

Seiches

Seiches are rhythmic fluctuations in the levels of lakes near the shores that somewhat resemble tides. The wind blowing over a body of water tends to pile up the water on the lee shore and lower the water level on the weather shore. This continues until

the wind has exerted its maximum force, after which the lake tends to return to a state of stable equilibrium. When the wind ceases the water which has accumulated on the lee shore falls below the mean level of the lake, while the water at the other end of the lake rises. Thus a series of rockings of the water of the whole lake takes place, the water at either end rising and falling alternately until a condition of rest is attained or until another wind starts the movement anew. This phenomenon is the same as may be observed in a basin of water where the water is disturbed slightly, moving from one side to the other before coming to rest. Other factors than the wind tend to produce these oscillations of water level, namely, differences in barometric pressure at the two ends of a lake, and differences of the temperature of the water. The wind, however, is by far the most important element in the problem.

In the Great Lakes the changes in level, due to the seiches, are often of considerable magnitude. They were carefully studied in Lake Erie by Professor A. J. Henry of the United States Weather Bureau in 1900 and described in Bulletin J of the Weather Bureau Publications. The fluctuations in the relative level in the water of the lake at Buffalo at the easterly end, and at Amherstburg, Ont., at the west end of the lake, were recorded by automatic gauges. Diagrams given in the report show that the surface of this lake is almost never at rest, but constantly rocks back and forth, the average time of oscillation being between 14 and 15 hours. These changes in level frequently amount to several feet, and in extreme cases to 10 or 12 feet or even more. Ordinarily, when the wind velocity is less than 25 miles per hour, the differences in level are not greater than one or two feet.

The storm of September 12th, 1900, with a velocity of 65 miles an hour for two hours, caused the water level at Buffalo to rise about 6 feet above its previous level, while at Amherstburg the surface of the water fell about 2 feet. Soon after the wind fell below its highest velocity, the lake level began to fall and continued to fall for nine hours, the amplitude of the oscillation being 7' 2" and the time being a little less than 16 hours. Professor Henry states that "the wind effect of this storm appears

to have been much the same as would have been produced by a quick powerful blow on the lake surface. The water of the whole lake was set in motion about a nodal line, and continued to rock for several days, the amplitude of each oscillation being a little less than that of the preceding one." Seiches of small amplitude occur even when the weather is not stormy, and in most of the large lakes minor fluctuations occur, the level of the lake rising and falling a few inches every 10, 20 or 30 minutes, as the case may be.

During the summer when the lakes become thermally stratified with a stratum of cold and relatively heavy water at the bottom and warm lighter water at the top, the seiches produced by the wind in the upper strata gradually transfer their motion to the heavier water beneath, so that this also acquires an oscillatory motion, the amplitude and period of which may be different from that of the surface seiche. These variable fluctuations tend to mix the water of the two strata in the region of the thermocline.

The seiches have an important influence on the undertow currents.

Vertical Currents

The water of the Great Lakes show, in general, the same fluctuations in the temperature of the water at the surface and at depths below the surface, as have been so frequently observed in smaller lakes and reservoirs. That is, during the summer the surface water is warmed by the sun, while the water at the depths is cold and quiescent. The wind stirs up the water of the lake and keeps it thoroughly mixed for a number of feet down from the surface. In small bodies of water the depth to which this wind action extends is seldom more than 20 or 30 feet, but in the large, deep lakes it is more. Observations made in Lake Erie at Cleveland in 1904, showed that the lake water was stirred by the summer winds to a depth of about 50 feet, while observations made in Lake Michigan in 1910 showed that the water was stirred to a depth of about 60 feet. Below the stratum within which circulation takes place, the temperature of the water changes rapidly and the region where this change occurs is

known as the thermocline. Below the thermocline the bottom water in the middle of the lakes probably remains relatively quiescent for long periods, but for several miles out from the shore the lower strata move in and out and are seldom at rest.

The temperature of the water at the bottom of the Great Lakes during the period of summer stagnation is practically that of maximum density, *i.e.*, 39.2° F. The author once measured the temperature at the bottom of Lake Champlain (396 feet) in June and found it to be 39.3°. Comparatively few observations of the temperature of the water at the bottom of the Great Lakes have been made, but they substantiate this statement. Recently observations in Lake Ontario near Rochester have shown that water of maximum density came within a mile and a half of the shore at a depth of 40 feet.

During the winter the surface water is colder than the bottom water. The latter maintains its temperature at about maximum density throughout the year.

During the spring, as well as during the fall, there is a period when the water has an opportunity to circulate from top to bottom. In very large lakes this period is short, and whether circulation actually extends to the bottom is not known.

Besides the vertical circulation produced by the natural heating and cooling of the surface water and the action of the wind, vertical circulation may also take place near the shore, due to the inflow of river water or sewage of a different temperature from the water of the lake. This sometimes has an important effect upon the manner in which these inflowing streams mix with the lake water.

Thermal stratification of the water in small lakes has an important effect upon the depth of the return currents above referred to, causing the back flow to take place above the layer of stagnant water. But in the Great Lakes the thermocline marks the dividing line between the upper and lower currents moving in opposite directions. It is an unstable thermocline and does not necessarily imply stagnation.

Local Wind Currents

From the standpoint of the pollution of water supplies, the most important currents that take place in the lakes are the local currents produced by the movement of the wind from day to day. As the wind blows over the lake surface currents of the water are induced by it, and as the wind changes, these currents also change. Observations that have been made in Lake Erie, notably by Walter P. Rice at Cleveland in 1890, and by the Cleveland Water Department in 1895, indicate that there is a fairly close relation between the wind movement and the movement of the surface water, the travel of the surface water being commonly from 4 to 6% of the wind movement and averaging about 5%. The movement of the water is less at depths below the surface, decreasing with the depth and presumably becoming zero at the neutral line, which recent studies in Lake Ontario have shown to be at mid-depth near the shore. Observations made in Owasco Lake near Auburn, N. Y., in 1911, by Mr. J. Walter Ackerman and the author, showed that the percentage which the travel of the surface water was of the wind movement varied with the velocity of the wind, being 3.2% when the wind velocity was 5 miles per hour, but only 1.2% when the velocity was 30 miles per hour. These observations were, however, made in a lake of relatively small size.

The velocities induced by the wind are greater on the lee shore than on the weather shore.

In order to illustrate the effect of these local currents induced by the wind, let it be assumed that the wind has been blowing off shore for 10 hours at the rate of 20 miles per hour in such a direction as to cause the water to flow from the sewer outfall towards the water supply intake, and let it be assumed further that the velocity of the surface water during this period was 3% of the wind movement. The surface water would, therefore, be carried 6 miles from the shore during the 10-hour period, a distance more than sufficient to carry it to the longest intake now in use.

In addition to the velocity of the surface water induced by the wind, it is important to know also the angle of dispersion.

An attempt was made to measure this at Cleveland in 1905. A group of floats was set adrift in Lake Erie, at a time when the wind was blowing at the rate of 13 miles per hour, and the position of each float observed for several hours. In one experiment after the floats had travelled 2,500 feet, which was 4.7% of the wind movement, they had spread through an angle of about 5%. In other experiments with higher wind velocities, the angle of dispersion was slightly less. At the present time no data exist showing the relation between wind velocity and the angle of dispersion. It varies widely according to the veering of the wind and may be as high as 30° or 60° more. After several days of variable winds the fan of polluted water may spread over a semi-circle.

Undertow Currents

When the wind blows strongly towards a lee shore the raised water level that results causes an outward current of the water beneath the surface. This phenomenon has long been familiar to fishermen and bathers. It has not been fully realized, however, that the undertow currents sometimes extend for several miles into the lake and well beyond the ordinary water supply intakes. As a result shore water is carried outward and sewage contaminated water periodically enters the intakes, and is pumped into the city mains. The best evidence of these undertow currents is obtained by a study of the temperature of the water at different depths, at different distances from the shore and of the temperature of the water drawn from the intakes.

Daily observations of the temperature of the water at Milwaukee and elsewhere during the summer have shown very great changes in the course of a few days. Thus at Milwaukee, the temperature of the water at the pumping was 68° on July 20th, 1910; on July 23rd it was 62°; and on July 27th, 52°. At Rochester, even more sudden changes have been noticed. For example, on August 8th, 1912, the temperature of the water at the bottom of the lake at a point 6,000 feet from the shore, where the depth was 40 feet, the temperature fell from 59° to 42° in eight hours, the surface temperature meanwhile remaining about 64°. Two days previous, at the same distance from the

shore, the temperature of the water had been 63° at all depths. The drop in temperature followed a sudden change in the direction of the wind from on-shore to off-shore.

The data now at hand indicate that the dividing line between the incoming and outgoing water lies at about mid-depth.

When the warm surface water is blown away from the shore and cold water flows landward near the bottom, not all of the bottom water flows in as far as the shore line. Some of it becomes mixed with the upper strata and returns to the lake before it reaches the shore line. The extent to which this off-shore mixing takes place has not yet been determined by adequate studies.

The undertow currents are of great importance in connection with the dispersion of sewage. During the summer season the temperature of the sewage will be ordinarily not far from that of the surface water of the lakes. If the sewage is discharged at the bottom of a lake at a considerable distance from the shore, it is obvious that when the cold, deep water is flowing shoreward, the sewage will be warmer and lighter than the water into which it is discharged. The sewage will, therefore, tend to rise into the upper strata and be carried away from the shore by the outward surface current. When the warm shore water is going out at the bottom the sewage will enter water of approximately its own temperature and will have less tendency to rise and will be carried away from the shore by the outward bottom current. Thus during the summer the movements of the wind, whether towards or away from the shore, tend at most times to carry the sewage away from the shore rather than towards it.

Lake Pollution

The principal sources of pollution of the lake water supplies are, first, sewage discharged directly into the lake along the water front. Second, sewage discharged into streams that flow into the lake. Third, sewage polluted mud dredged from rivers and harbors and dumped into the lake. Fourth, sewage sludge transported by ice from the shore outward. Fifth, fecal matter discharged into the lake from boats.

The danger of pollution of the water supply in any case depends upon the opportunities afforded for the commingling of the sewage with the water before it reaches the intake, and upon the natural purification that takes place in the lake.

Dispersion of Sewage in Lake Waters

When sewage is discharged into a lake it mingles with the water and gradually becomes dispersed through it, the nature and extent of the dispersion being dependent upon the local currents induced by the wind. It is impossible to calculate exactly the dilution of the sewage at different distances from the sources of pollution, for there are too many unknown factors, but computations based on arbitrary assumptions are sometimes found useful in showing approximately the dilution that may be expected under different conditions.

For example, suppose that sewage is being discharged at a point off shore and is dispersed through a sector that has an angle θ ; and suppose, for purposes of calculation, that the sewage mixes through the entire depth and that this depth is constant. Let Q stand for the quantity of sewage discharged in time t ; let r = the distance travelled by the water, under the influence of the wind in the same time, i.e. let r be the radius of the sector; and let d be the depth. If D represent the dilution, then

$$\text{After time } t \quad D_t = \frac{\pi r^2 d}{Q} \frac{\theta}{360}$$

$$\text{After time } 2t \quad D = \frac{3\pi r^2 d}{Q} \frac{\theta}{360}$$

$$\text{After time } nt \quad D_{nt} = \frac{(2n-1)\pi r^2 d}{Q} \frac{\theta}{360}$$

To apply this to a practical case, suppose that sewage is being discharged at the rate of 25 million gallons per day; that the depth of water is 50 feet; that the wind movement is 100 miles per day and the water travel 5% of this, or 5 miles per day; that the angle of dispersion is 5° ; and that t is one minute. Then $Q = 2320$ cubic feet per minute and $r = 18.3$ feet per minute.

$$D_{nt} \frac{(2m-1) \times 3.1416 \times 18.3^2 \times 50}{2320} \frac{5}{360} = .315 (2N-1)$$

Suppose that the sewage contains 1,000,000 bacteria per cc. and the water none. Then for different distances from the point of discharge the water would contain the following numbers of bacteria:

| r | n | D | Bacteria per cc. |
|----------|---------|-------|------------------|
| 100 feet | 5.46 | 3.13 | 320,000 |
| 500 " | 27.3 | 16.80 | 59,600 |
| 1,000 " | 54.6 | 34.1 | 29,300 |
| 2,000 " | 109.2 | 68.4 | 14,600 |
| 3,000 " | 163.8 | 103.0 | 9,700 |
| 4,000 " | 218.4 | 137.2 | 7,300 |
| 5,000 " | 273.0 | 171.5 | 5,900 |
| 6,000 " | 327.6 | 203.0 | 4,900 |
| 7,000 " | 382.2 | 241.0 | 4,200 |
| 10,000 " | 546.0 | 344.0 | 2,900 |
| 15,000 " | 819.0 | 516.0 | 1,900 |
| 20,000 " | 1,092.0 | 669.0 | 1,500 |

For different angles of dispersion the following numbers of bacteria would be found at different distances from the point of discharge:

| Distance from Point of Discharge in Feet | Number of Bacteria per cc. | | | |
|--|----------------------------|---------|--------|--------|
| | 5° | 10° | 30° | 60° |
| 100 | 320,000 | 160,000 | 53,000 | 27,000 |
| 500 | 59,600 | 29,800 | 10,000 | 5,000 |
| 1,000 | 29,300 | 14,700 | 4,900 | 2,900 |
| 2,000 | 14,600 | 7,300 | 2,400 | 1,200 |
| 3,000 | 9,700 | 4,800 | 1,600 | 800 |
| 4,000 | 7,300 | 3,700 | 1,200 | 600 |
| 5,000 | 5,900 | 3,000 | 1,000 | 500 |
| 10,000 | 2,900 | 1,500 | 480 | 240 |
| 15,000 | 1,900 | 950 | 320 | 160 |
| 20,000 | 1,500 | 750 | 250 | 125 |

Natural Agencies of Purification in Lake Waters

In addition to the very great and rapid dispersion of sewage in the water of the Great Lakes, various other agencies tend to bring about its natural purification.

Sedimentation is a potent factor. Compared with streams the velocities of the water in the lakes are low, so that, except near the shore, the suspended matter settles to the bottom, leaving the upper broad waters of the lake very clear. Sedimentation must always be considered, however, with reference to subsequent disturbances of the settled solids by currents. During long periods of quiescence, pathogenic bacteria are liable to natural death in an unfavorable environment.

According to the best available information, the germs of typhoid fever do not multiply in the waters of the lake, but rather disappear at rates that vary according to different conditions. Using approximate figures for the sake of illustration it may be said that after a week ninety per cent of any typhoid fever germs that may enter one of the lakes will have died, and after a month 99 per cent. How long the most resistant germs can survive is quite unknown. A small number, sometimes termed the "resistant minority," doubtless remain alive for several months. They are able to live longer in cold water than in warm water, a fact that Houston has recently demonstrated by some interesting experiments.

Sunlight exerts a powerful germicidal action on the bacteria in the layers of water near the surface, but even in the waters of a clear lake the sun's rays rapidly lose their energy below the surface, so that disinfection by sunlight is not a factor at depths greater than a few feet.

Very important, however, is the action of the microscopic organisms found in the waters of all the lakes and that comprise the "plankton." The biological cycle is wondrously complete. Particles of sewage solids are decomposed by bacteria; bacteria are consumed by the protozoa; protozoa are consumed by rotifers and crustacea and the latter are eaten by fish. Also the products of bacterial action on the dispersed sewage, such as nitrates and carbonic acid, furnish food for the algae, such as floating diatoms and various chlorophyceæ, and these in turn furnish food for the crustacea and larger organisms.

The oxygen resources in the Great Lakes are so enormous that except very near to the sources of pollution the lake water is saturated with dissolved oxygen. The complete destruction

of the organic matter of the sewage by oxidation is, therefore, the ultimate fate of all sewage matters that enter the lakes.

Observed Contamination of Lake Water by Sewage

Systematic analyses of the lake water in the vicinity of Milwaukee, Chicago, Cleveland, Toronto and Rochester have given results not inconsistent with computation similar to the preceding. In general, they have shown that the dilution of sewage discharged into the lakes is ordinarily very great. It is, however, very variable and under certain conditions that occur several times each year, the sewage is projected through the lake water for several miles with relatively little dilution. When the path of this sewage stream lies in a direction from the sewer outfall to the water works intake, contamination of the water supply may and does occur.

The analyses that have proved most serviceable in the study of this problem are the following: (1) Number bacteria per cc. (2) Test for *B. coli*. (3) Turbidity. (4) Odor. (5) Chlorine.

The relative sensitiveness of these determinations varies according to the nature of the sewage. Ordinarily the bacterial tests are the most sensitive, but not infrequently the simple odor test is equally satisfactory.

As an illustration of the observed contamination of lake water by sewage, mention may be here made of the studies conducted by the Milwaukee Sewerage Commission during the summer of 1910.

The sewage of Milwaukee, which then amounted to about 60 million gallons per day, is practically all discharged into the lake at the mouth of the Milwaukee River. Thence it spreads outward through the lake water and covers a fan-shaped area, becoming diluted as it leaves the shore. The water at the mouth of the river was found to contain very large numbers of bacteria, the average being 1,268,000 per cc., the minimum 525,000, and the maximum 2,600,000 per cc. The following figures show the observed numbers of bacteria at different distances from the shore along a line extending outward into the lake from the river mouth.

Average Number of Bacteria in Lake Michigan Water at
Different Distances from the Shore Opposite the
Mouth of the Milwaukee River

| Location | Bacteria per cc. |
|----------------------------|------------------|
| Mouth of River | 1,268,000 |
| 1 mile east of river mouth | 207,000 |
| 2 miles " " " " | 2,000 |
| 3 miles " " " " | 970 |
| 4 miles " " " " | 225 |
| 5 miles " " " " | 45 |

The water supply intake is about 3.5 miles in a straight line northeast of the river mouth. Here the average number of bacteria was 1,182 per cc. at the surface and 693 per cc. at the bottom, the largest numbers being 3,720 at the surface and 1,600 at the bottom, and the smallest numbers being 20 at the surface and 50 at the bottom. Generally speaking, the bacteria were higher at the surface than at the bottom, but sometimes the opposite was the case.

The observations of the Commission covered samples of water collected at intervals of one mile along a series of lines one mile apart from the shore outwards for three or four miles. Several series of samples were collected with the wind blowing in different directions. The results showed what would be naturally expected,—that the greatest amount of pollution could be traced in the direction towards which the wind was blowing. At times the axis of greatest pollution extended in a northeasterly direction towards and beyond the intake. At other times the course of the sewage was southerly.

Tests for *B. coli* were made on all of the samples of water collected, and estimates made of the average number present at each station. Thus at the mouth of the river the estimated average number of *B. coli* was 847 per cc. The numbers decreased outward from the shore, until at a point five miles from the shore the water contained less than one *B. coli* per cc. At the intake of the water works, the number was 2.1 per cc. at the surface and 0.4 per cc. at the bottom.

A study of the *B. coli* tests showed in a striking way the effect

of the on-shore winds in causing the polluted water to pass out into the lake at the bottom and the effect of the off-shore winds in causing it to spread out over the surface. Thus, taking all of the samples collected at points more than a mile away from the shore, it was found that when the wind was blowing towards the shore the bottom water contained four times as many *B. coli* as the surface water, but that when the wind was blowing off shore the surface water contained eight times as many *B. coli* as the bottom water.

The effect of the sewage of the city on the bacterial character of the water at the intake and the variations from day to day are shown by the following daily analyses:

DAILY ANALYSES OF WATER AT THE NORTH POINT PUMPING STATION

| Date 1910 | Hour p.m. | Temper- ture Fahr. | Turbid- ity | Color | Odor | Chlorine | Bacteria per cc. | Test for <i>B. Coli</i> | | |
|--------------|--------------|--------------------------|----------------|-------|------|----------|---------------------|-------------------------|-------------|--------------|
| | | | | | | | | 0.1 c.c. | 1.0 c.c. | 10.0 c.c. |
| Sept. 21... | 4.50 | 57.8 | 2 | 2 | 1v | 4.0 | 2000 | 0 | + | + |
| 22... | 3.55 | 58.0 | 2 | 3 | 1v | 4.2 | 1500 | 0 | + | + |
| 23... | 4.05 | 58.3 | 6 | 9 | 2v | 4.0 | 1270 | + | + | + |
| 24... | 4.10 | 58.1 | 14 | 4 | 1v | 4.5 | 1310 | + | + | + |
| 25... | 5.00 | 57.9 | 6 | 2 | 1v | 4.2 | 1270 | + | + | + |
| 26... | 4.45 | 58.0 | 12 | 7 | 3d | 4.2 | 1940 | + | + | + |
| 27... | 3.55 | 57.9 | 4 | 2 | 2m | 4.0 | 2065 | + | + | + |
| 28... | 2.50 | 57.8 | 7 | 4 | 2v | 4.0 | 1820 | + | + | + |
| 29... | 4.25 | 57.8 | 4 | 3 | 1v | 4.0 | 1750 | + | + | + |
| 30... | 4.10 | 57.0 | — | — | — | — | 1100 | 0 | 0 | + |
| Oct. 1... | 4.20 | 57.1 | 5 | 4 | 1v | 4.2 | 3000 | + | + | + |
| 2... | — | — | — | — | — | — | — | — | — | — |
| 3... | 4.00 | 53.2 | 6 | 2 | 1v | 4.0 | 2300 | + | + | + |
| 4... | 3.30 | 52.5 | 6 | 3 | 1v | 4.8 | 940 | + | + | + |
| 5... | 1.58 | 47.0 | 4 | 4 | 1v | 4.2 | 1250 | + | + | + |
| 6... | 3.50 | 56.5 | 10 | 4 | 2m | — | 3500 | 0 | + | + |
| 7... | 4.40 | 56.0 | 7 | 2 | 2v | 4.0 | 825 | 0 | + | + |
| 8... | 4.00 | 53.7 | 6 | 2 | 1v | 4.2 | 1315 | 0 | + | + |
| 10... | 4.30 | 55.3 | 5 | 2 | 1v | 4.2 | 1250 | + | + | + |
| 11... | 2.10 | 46.4 | 6 | 2 | 1v | 4.0 | 500 | 0 | + | + |
| 12... | 3.40 | 53.4 | 20 | 4 | 1v | 4.0 | 900 | 0 | + | + |
| 13... | 11.35am. | 54.3 | 15 | 4 | 1v | 4.0 | 870 | 0 | + | + |
| 14... | 3.00 | 53.5 | 10 | 3 | 1v | 4.0 | 345 | 0 | + | + |
| 15... | 5.20 | 54.8 | 4 | 2 | 1v | 4.5 | 330 | 0 | + | + |
| 17... | 2.40 | 54.9 | 5 | 5 | 1v | 4.0 | 5900 | + | + | + |
| 18... | 4.45 | 54.7 | 3 | 3 | 2v | 4.2 | 800 | 0 | + | + |
| 19... | 12.05 | 54.1 | 6 | 3 | 1v | 4.2 | 1200 | 0 | + | + |
| 20... | 4.20 | 54.5 | 15 | 4 | 2m | 4.0 | 1215 | 0 | + | + |
| 21... | 3.55 | 54.0 | 10 | 3 | 2v | 4.0 | 680 | 0 | 0 | + |
| 22... | 3.45 | 53.3 | 20 | 5 | 2v | 4.0 | 1950 | 0 | + | + |
| 24... | 2.25 | 53.0 | 8 | 3 | 1v | 4.0 | 2750 | + | + | + |
| 25... | 3.35 | 53.3 | 12 | 2 | 1m | 4.5 | 1025 | 0 | + | + |

1v = very faint vegetable

2v = faint vegetable

2m = faint moldy

3d = distinct disagreeable

Contaminated Lake Water Supplies and the Public Health

Stronger proof than that furnished by analysis is the effect of the use of contaminated water on the public health measured by vital statistics. A very complete study of the death-rates from typhoid fever and other diarrhoeal diseases in the cities that take their water supplies from the Great Lakes has been recently published by Dr. Allan J. McLaughlin in the form of two bulletins (Nos. 77 and 83 of the Hygienic Laboratory of the Public Health and Marine Hospital Service of the United States) entitled "Sewage Pollution of Interstate and International Waters with Special Reference to the Spread of Typhoid Fever." These reports describe the water supply and sewerage conditions in each of the lake cities and give tables of vital statistics compiled from local sources and from data gathered by the U. S. Census Bureau. The statistics are illustrated by many diagrams.

The case made out against the lake cities that do not filter their water supplies is a strong one. The typhoid fever death rates are shown to be very high as compared with European cities and with the cities of the United States that have safe water supplies. As an illustration of these high rates the following table, compiled from the United States Census reports, is presented on page 296.

Dr. McLaughlin points out that in the lake cities that use unfiltered water the typhoid fever death rate is exceptionally high during the winter season, thus affording additional evidence that this disease is more often transmitted by cold water than by warm water. He also shows that intestinal diseases classed as diarrhoea and enteritis, and infantile diseases are exceptionally prevalent in the lake cities that use unfiltered water and they too are liable to occur in the winter under the name "winter cholera."

In view of the completeness and accessibility of his reports, it is unnecessary to discuss this subject in detail.

TYPHOID FEVER DEATH-RATES OF CERTAIN CITIES SUPPLIED WITH WATER FROM
THE GREAT LAKES

(Data from United States Census Reports)

| City | Population 1910 census | Typhoid Fever Death-rate per 100,000 | | | | | | | | |
|-----------------------------|------------------------------|--------------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | | 1901 | 1902 | 1903 | 1904 | 1905 | 1906 | 1907 | 1908 | 1910 |
| Lake Superior | | | | | | | | | | |
| Duluth, Minn..... | 78,466 | 74.1 | 53.7 | 64.8 | 54.4 | 44.7 | 46.0 | 41.6 | 56.8 | 52.3 |
| Marquette, Mich..... | 11,503 | 19.6 | 57.9 | 28.5 | 37.5 | 37.0 | 36.5 | 71.9 | 44.4 | 52.5 |
| Lake Michigan | | | | | | | | | | |
| Chicago, Ill..... | 2,185,283 | 29.8 | 45.1 | 32.1 | 20.1 | 16.5 | 18.3 | 17.7 | 15.3 | 12.6 |
| Milwaukee, Wis..... | 373,857 | 22.1 | 15.1 | 16.8 | 13.6 | 22.7 | 30.5 | 25.7 | 17.4 | 21.2 |
| Muskegon, Mich..... | 24,062 | 19.2 | 13.4 | 19.2 | 28.7 | 28.7 | 33.4 | 14.3 | 33.4 | 24.8 |
| Michigan City, Ind..... | 19,027 | 13.1 | 31.9 | 68.4 | 54.6 | 35.5 | 34.7 | 50.8 | 48.9 | 27.0 |
| Marinette, Wis..... | 14,610 | 31.2 | 31.5 | 51.0 | 25.8 | 39.1 | 26.3 | 40.0 | 13.5 | 25.0 |
| Escanaba, Mich..... | 13,194 | 50.3 | 67.8 | 28.0 | 351.4 | 182.8 | 101.1 | 220.2 | 126.5 | 230.0 |
| Traverse City, Mich..... | 12,115 | 30.4 | 19.4 | | | 25.7 | 90.5 | 23.8 | 53.6 | 29.6 |
| Menominee, Mich..... | 10,508 | 56.5 | 25.1 | 86.8 | 117.2 | 46.9 | 78.2 | 91.8 | 64.0 | 54.5 |
| Lake Huron | | | | | | | | | | |
| Bay City, Mich..... | 45,166 | 25.3 | 36.2 | 54.3 | 43.4 | 24.6 | 49.3 | 41.9 | 49.3 | 35.9 |
| Port Huron, Mich..... | 18,863 | 41.3 | 61.2 | 25.2 | 34.9 | 14.8 | 53.8 | 43.5 | 19.1 | 52.1 |
| Sault Ste. Marie, Mich..... | 12,615 | 92.9 | 172.9 | 115.9 | 52.4 | 68.6 | 58.9 | 16.5 | 72.9 | 56.1 |
| Lake Erie | | | | | | | | | | |
| Cleveland, Ohio..... | 560,663 | 34.9 | 35.5 | 115.0 | 49.6 | 14.9 | 20.2 | 18.9 | 12.6 | 13.4 |
| Buffalo, N. Y..... | 423,715 | 27.1 | 33.7 | 34.6 | 24.2 | 24.4 | 23.6 | 29.2 | 20.7 | 23.8 |
| Detroit, Mich..... | 465,766 | 20.1 | 23.5 | 20.0 | 17.6 | 21.2 | 22.3 | 28.3 | 22.3 | 20.5 |
| Eric, Penn..... | 66,525 | 16.7 | 25.4 | 33.7 | 48.6 | 17.0 | 48.3 | 78.4 | 62.5 | 29.0 |
| Ashtabula, Ohio..... | 18,266 | 44.9 | 36.3 | 49.4 | 137.1 | 60.0 | 38.9 | 19.0 | 86.2 | 42.0 |
| Dunkirk, N. Y..... | 17,221 | 24.3 | 76.6 | 50.9 | 41.4 | 46.1 | 37.7 | 72.2 | 11.5 | 5.9 |
| Lake Ontario | | | | | | | | | | |
| Toronto, Ont..... | 208,040 ^a | 17.8 | 14.3 | 18.2 | 25.8 | 18.7 | 31.4 | | | |
| Niagara Falls, N. Y..... | 30,455 | 143.9 | 130.4 | 126.9 | 139.8 | 181.6 | 147.3 | 126.6 | 98.0 | 87.5 |
| Kingston, Ont..... | 17,691 ^a | 39.0 | 5.5 | 99.5 | 22.1 | 38.5 | 38.4 | | 23.1 | 34.8 |

WATER SUPPLY INTAKES

The lakes are the natural sources of water supply of the cities and towns near them, and in some instances they are the only possible sources. The land around the lakes is generally flat and

^a Census of 1901.

no upland gravity supplies are obtainable. A few places, like Toledo, are supplied with water pumped from streams entering the lakes, but in most instances water of better quality and of unlimited volume is found in the lakes themselves. The fact that the supply is unlimited, or rather is limited only by the capacity of the pumps installed, seems to have encouraged a lavish use and waste of water, for we find that the per capita consumption of water in the lake cities has been high. The fact that the water is relatively cool in summer has, in some cases, developed a unique use of the water supply for cooling purposes. In recent years a number of unsuccessful attempts have been made to cut down the consumption.

The broad waters of the lake cannot be used for water supplies as it is not practicable to extend intake pipes or tunnels to points where the depth of water much exceeds 75 feet. The longest intake in use is that at Cleveland, which is 26,000 feet long and the end of which is about four miles from the shore. The Chicago intakes are from two to four miles long. The intakes at Milwaukee, Gary and Oswego are about a mile and a half long. There are several intakes about a mile long, namely, those at Bay City, Ashland, Kanawha, Sheboygan, Evanston, Racine and Erie. Many of the intakes are shorter than this extending from 1,000 to 3,000 feet from the shore, and in some cases they are less than 1,000 feet.

Comparatively few intakes are located in water more than 50 feet deep. One of the deepest is that at Duluth, where the water is 75 feet deep and the openings in the crib 60 feet below the surface of the water. The Toronto intake extends into water 68 feet deep, and it is proposed to extend it to water 100 feet deep. Oswego is constructing an intake in 83 feet of water. The Milwaukee intake is in 60 feet of water and the Chicago intakes are in from 27 to 40 feet of water.

The attempt seems to have been made in every case to extend the intake far enough to obtain relatively clear water and avoid pollution of the intake from local sewers. How inadequately the latter has been accomplished is shown by the typhoid fever statistics elsewhere quoted. Other considerations have been to have the intake in water deep enough to avoid a packing of the

ice around the crib in the winter and to avoid the silting and clogging of the intake and pipe through movements of the sand. It has ordinarily been found desirable to have a depth of 20 or 30 feet.

The intakes at Cleveland and Chicago terminate in masonry cribs that extend above the water and are surmounted by light-houses. These cribs have entry ports at different depths. More often the intake pipes terminate in a submerged crib, or the pipe is merely turned up and supported by loose rock. Cast iron pipe has been largely used in the past but steel is gradually taking its place. Tunnels are used at Chicago, Cleveland and elsewhere.

Many breaks have occurred in the lake intakes and a recital of the accidents would be interesting. In several notable instances, as at Toronto, these accidents have permitted polluted shore water to enter the pipes and outbreaks of disease have followed.

Methods of Protecting Lake Water Supplies

The evidence is conclusive that natural methods of purification cannot be depended upon to protect the sanitary quality of the water supplies taken from the Great Lakes. Practically every city, whether great or small, that has depended solely upon the protection afforded by dilution and a supposedly remote location of the intake from the sewers has suffered from water-borne diseases. As a rule the smaller cities have suffered more than the large cities as their water supply intakes and sewer outfalls are nearer together. The visitations of typhoid fever have often been intermittent, and their failure to occur at regular seasons engenders a false sense of security; but sooner or later, when the necessary combination of currents and infection occurs, every lake city that fails to protect its water supply is bound to suffer from water-borne diseases.

Various expedients have been used at different times and at different places. At Chicago, after it became certain that its water supplies were subject to sewage pollution in different degrees according to the weather conditions the Health Department of the city inaugurated the policy of making daily analyses

and issuing notices of the condition of the water in the daily papers, warning the people to boil the water or to cease using it for drinking in case the analysis was bad. This was many years ago. The practice may have had some beneficial effect, but it was placing dependence upon a frail reed. It had the inherent disadvantage that the quality of the water changed more rapidly than the analyses could be made and published.

A second method of protection would be to abandon the lake water altogether and substitute some other source of supply. This has been considered in some cities, as for example, at Toronto, where a gravity supply has been considered and rejected. Most of the lake cities are so situated that another source of supply is impracticable, or, in any event, costly, so this course has not been adopted and is not likely to be.

A third method is to extend the intake further into the lake. This has been done repeatedly. As the cities have grown the local pollution has become heavier and larger intakes have been required on account of greater water consumption. The effect of using longer intakes farther removed from sources of pollution has invariably improved the condition of the water, sometimes very noticeably. After a time the water at the new intakes becomes contaminated so that the remedy is merely of temporary benefit. Then, too, there is a limit to which this can be carried as the water off shore becomes too deep for economical pipe laying.

A fourth method would be to keep the sewage out of the lake. This is practically impossible, as the natural drainage of the lake cities is towards the shore. Ordinarily no attempt has been made to keep the sewage out.

Chicago presents the only important instance where it has been accomplished and here it has not been accomplished in full. Situated at the south end of Lake Michigan and with only a low divide between it and the streams that flow westerly into the Mississippi River basin, and with this divide near at hand, it was possible to cut a canal through the divide, and turn the flow of the principal sewers into it, so that the sewage would flow westerly. This project, known as the Chicago Drainage Canal, cost upwards of forty million dollars and entails a con-

siderable annual charge for maintenance. A city of small size could have not financed so great an undertaking. The canal is so arranged that the Chicago River and its branches now discharge into it instead of into Lake Michigan; the lake water flows in at the old river mouth and dilutes the sewage, also turned from the lake into the river. The canal extends to Lockport, where the diluted sewage is discharged into the Des Plaines River, which flows into the Illinois River, this in turn flowing into the Mississippi River. The use of this canal led to a notable suit in the U. S. Supreme Court, brought by the State of Missouri, acting in the interest of St. Louis, against the State of Illinois and the Chicago Drainage Canal District, which was settled in favor of Chicago.

This canal receives most, but not all of the sewage of the city. In the southern part of the city there are large sewers that still discharge into the lake and pollute its waters. Projects are now in contemplation that will divert much of this sewage westward into the canal. It is recognized, however, that this method of diversion and dilution has a limit and that this limit will be exceeded before many years, so that projects are also being considered for the treatment of the sewage before it is discharged into the canal.

The Chicago Drainage Canal has very materially reduced the amount of typhoid fever in the city. It has not entirely prevented all pollution of the water supply. The large storm flows of the sewers still go in to the lake and at certain times this may affect the water supplies from the various cribs. Furthermore, the accidental contamination of the lake water from so large a city with its shipping, its dredging operations, its industries located along the shore, is by no means a negligible factor. To protect the lake water against all these is a difficult task, except by filtration.

Protection by Sewage Treatment

The next method of protection to be considered is the purification of the sewage before it is discharged into the lake. This has long received the attention of engineers and so much has been said about it in popular writings that the public has come

to have faith in it. It is a plausible idea, and theoretically sound, but it has one fatal defect. To accomplish the purification of all of the sewage at all times demands works of excessive cost, while to partially purify the sewage, or to fail to purify it at times of storm does not give the desired protection to the water supply. Nearly all large cities are sewered on the combined system, that is, the same pipes and conduits carry both house sewage and storm water. Purification works large enough for the treatment of all the storm water as well as the house sewage are almost never constructed, but overflows are provided to take the excess sewage at times of heavy rain. This storm overflow is merely the house sewage diluted and from a sanitary standpoint is dangerous. The storms that produce the overflow are likely to be accompanied by strong winds that create rapid and direct currents of the water in the lake, so that the method of protection by sewage treatment fails at those times when it is most needed.

The term "sewage purification" has been frequently used to cover methods of sewage treatment that only partially purify and that do not yield satisfactory effluents, considered from a sanitary standpoint. For example, it has been applied to screening, to sedimentation, to septic tanks, to chemical precipitation, to the use of contact beds, etc., processes which are often of great merit in their proper field, but which do not by any means convert sewage into drinking water, or into a liquid that can be safely mixed with drinking water. The misuse of the term "sewage purification" has thus led laymen to the belief that a lake water could be protected simply by "purifying" the sewage. The more recent use of the term "sewage treatment" instead of "sewage purification" should help to disabuse the mind of the public in this regard.

Treatment of the sewage of lake cities is often desirable in order to prevent objectionable conditions in the lake water near the point of discharge, and some form of treatment is likely to be adopted by nearly all of them. The nature of the treatment required will be usually governed by conditions other than the protection of the water supply. These treatments will, at the same time, somewhat reduce the danger of the pollution of the

water supplies and will serve as an additional factor of safety. The point here emphasized is that in themselves, they are not sufficient to protect the water supplies.

The disinfection of the sewage by the use of chloride of lime has been suggested and if this could be carried out thoroughly the safety of the sewage effluent would be materially enhanced. The cost of disinfecting sewage, however, would be much greater than the cost of disinfecting the water supply, so that, if disinfection were to be depended upon, the latter would naturally be preferred. The difficulty of disinfecting the overflow sewage at times of storm is another very great objection to this method. Used in connection with other forms of sewage treatment disinfection would further increase the factor of safety, but it ought not to be depended upon alone to protect the lake water supplies.

DISINFECTION OF LAKE WATER

If nature's methods of purification cannot be depended upon, if in the present state of the art an adequate purification of all the sewage is impossible of attainment, and if a partial treatment of the sewage does not suffice, the only course left is to purify the water supply itself. Fortunately this can be done satisfactorily and at reasonable cost. There are two methods of purification available for lake waters at the present time,—disinfection and filtration.

The disinfection of the lake water supplies has been extensively practiced during the last few years. Among the larger cities where it has been used may be mentioned Toronto, Milwaukee, Cleveland, Erie and Niagara Falls. Chloride of lime, or bleaching, has been chiefly used, but at Cleveland liquid chlorine was tried with success.

The fact that the lake waters contain relatively small amounts of organic matter as compared with other surface waters enables disinfection to be accomplished by the use of small quantities of chemicals. For the same reason the use of an excess of chemicals is readily noticed by the consumers on account of the disagreeable odor of chloride of lime that persists until the water reaches the service taps. Great caution is, therefore, required in the

use of this method. If too little bleaching powder solution is added the disinfection will not be effective, while if too much is added the water will have a bad odor. The quantities of bleaching powder used have varied from 6 to 18 pounds per million gallons. (10 pounds of calcium hypochlorite, containing 35% of available chlorine, per million gallons of water is equivalent to 0.42 parts per million of available chlorine.) Generally the smallest quantity found necessary to give effective sterilization of the water has been 6 to 8 pounds per million gallons. Quantities larger than about 10 pounds commonly leave undecomposed hypochlorites in the water that may be detected by the consumers.

It is of the greatest importance to secure a prompt and intimate mixture of the bleaching powder solution with the water. This is not as easily accomplished as many think and requires a degree of skill in operation not easily obtained in practice. Failure to properly apply the chemical may easily escape knowledge of the authorities and such failure may be calamitous in its results.

That effective sterilization of the water can be obtained by this method is admitted by sanitarians; that it actually is obtained with practice is more doubtful. As an illustration of its results in a scientifically controlled plant the experience of Erie may be cited.

After the severe epidemic of typhoid fever that occurred in Erie during the first four months of 1911, a disinfecting plant was installed. During the first few weeks of operation, namely, from March 15th to April 25th, the numbers of bacteria in the treated water did not exceed 50 per cc. and averaged only 7 per cc. During this period from 7 to 10 lbs. of bleaching powder per million gallons of water were used. Later this was reduced to 6 to 8 lbs. The average numbers of bacteria per cc. in the raw and treated waters during subsequent months were as follows:

| Month | Year | Bacteria per cc. | |
|--------|------|------------------|---------------|
| | | Raw Water | Treated Water |
| March, | 1911 | 200 | 5 |
| April, | 1911 | 225 | 10 |
| May, | 1911 | 495 | 160 |
| June, | 1911 | 505 | 165 |

| Month | Bacteria per cc. | |
|-----------------|------------------|---------------|
| | Raw Water | Treated Water |
| July, 1911 | 165 | 35 |
| August, 1911 | 295 | 50 |
| September, 1911 | 215 | 35 |
| October, 1911 | 380 | 35 |
| November, 1911 | 500 | 45 |
| December, 1911 | 400 | 35 |

No *B. coli* were found in the treated water.

That the use of bleaching powder as a water disinfectant has reduced the typhoid-fever death-rates in many places is probable, but its use has not been continued long enough to enable this to be measured with great certainty. That it does not completely protect against water-borne diseases is also probable. Thus, at Toronto, the water supply was disinfected before the recently constructed filter was put into use. During this period, it is said that the typhoid fever death rate fell considerably below what it had been when untreated water was supplied, but after the filter was put into operation there was a further reduction of the death-rate, showing that disinfection alone had not furnished complete protection.

The method of disinfection of lake supplies ought to be looked upon not as a means of permanent protection of the quality of the water, but rather as a temporary or emergency measure. The uncertainties of operation are too great, the chances that not all bacteria are killed are too large to make this method one to be depended upon solely and permanently. And it is doubtful if the consumers will be long satisfied with water that may at any moment run from the service taps with an odor of chloride of lime. In the case of supplies that are only slightly contaminated it may be used to reduce still further the chance of infection, and thus, perhaps, postpone the time when filters are required, but such instances are few.

FILTRATION OF LAKE WATER

The best method of protecting the lake water supplies is to filter the water. This is more efficient than disinfection of the water and is very much cheaper than purification of the sewage.

Disinfection of the water does not remove any turbidity that may be present; filtration does. Disinfection does not remove any odor that may be present due to algae; filtration, with aeration, does this, and while it is not often a matter of great moment, at times it may be of decided benefit. Therefore, although filtration costs more than disinfection, it gives more effective service and is more dependable.

Two methods of filtration are in use in the lake cities,—sand filtration and mechanical filtration. These are now so well known that they do not need to be described. Suffice it to say that sand filters are operated at relatively low rates, say from 2 to 6 million gallons per day, and that mechanical filters employ a rate of about 125 million gallons per day. Sulphate of alumina, or some other coagulant, is employed with mechanical filters.

The choice of the two systems should be determined for each case according to the character of the water to be filtered, the availability of filter sites at proper elevation, and other local conditions. Generally speaking, sand filters are especially applicable to relatively clear waters and mechanical filters to waters that are turbid for a considerable portion of the time. In general, practice has followed this classification. Mechanical filters have been used by a number of the cities on the south shore of Lake Erie, as, for example, Lorain, Elyria, Vermillion, Sandusky, Conneaut and Ashtabula. Here the intakes are rather near the shore and the water is somewhat turbid. A mechanical filter is now being designed for Evanston for the same reason, namely, that the shore water is turbid. At Toronto on the other hand, where the turbidity is seldom high, a sand filter has been recently constructed and is now in operation. In a few instances mechanical filters have been installed to purify relatively clear lake waters, namely, at Niagara Falls on the Niagara River, and at Burlington, Vt., on Lake Champlain. Such filters are at a disadvantage from the standpoint of opera-

tion in that the attendant cannot as readily tell how the filter is working, for the reason that there is little difference in the appearance of the water before and after filtration. In the case of turbid or colored water, this difference is conspicuous, and failure to obtain perfect clarification is an indication of poor efficiency. Mechanical filters with clear waters have not been operated long enough to enable one to fairly judge of their success. It has been found that the quantity of alum necessary to be used with a mechanical filter operating on a clear water cannot be reduced much below $\frac{3}{4}$ grain per gallon without impairing the bacterial efficiency.

With clear lake waters the rate of sand filtration may be higher than in the case of other surface waters. The Toronto filter, for example, was designed for a rate of 6,000,000 gallons per acre per day, and when operated at this rate satisfactory bacterial efficiencies have been obtained.

Although sand filters cost somewhat more to construct than mechanical filters, this difference is not great and their cost of operation is less, so that when interest charges, operation and depreciation are all taken into account, the cost of the sand filtration may be less than that of mechanical filtration, while on the whole the results are more dependable as less skill is required in operation. Good results, however, can be obtained by either method. Both mechanical filters and sand filters need to be faithfully operated and enlarged when necessary, in order that their capacity may not be overtaxed. Failure to do so may involve serious trouble. For example, the sand filter at Ashland, Wis., is said to have been overtaxed to such an extent that filtration became imperfect and typhoid fever increased in the city. At Lorain, Ohio, faulty operation of the mechanical filter likewise caused an increase of typhoid fever in 1903.

In order to furnish an additional safeguard against infection of the water, it is becoming customary to provide for the disinfection of the water after filtration so that if for any reason the process of filtration has to be suspended, or if the bacterial efficiency falls below what it should be, hypochlorite may be used.

With the water supply filtered, expensive treatment of the sewage discharged into the lake is usually unnecessary. In fact,

in some cases no purification may be required so far as the protection of the water supply is concerned. Treatment of the sewage, of course, gives an additional factor of safety.

The Problem a Local One

The problem of protecting the water supplies of the lake cities is primarily and distinctly a local one. Each city is guilty of polluting its own water supply and each city is innocent of polluting the water supplies of its neighbors. There are perhaps a few minor exceptions and these are chiefly on the streams connecting the lakes. For example, the water supply of Detroit is somewhat polluted by the sewage of other places on the Detroit River, and the water supply of Niagara Falls is badly polluted by the sewage of Buffalo. As an example of a lake city that slightly pollutes the water of its neighbors may be mentioned Milwaukee, where the drift of polluted water extends as far as Cudahy, but even the Cudahy supply is polluted more by its own sewage than by that of Milwaukee.

Each city also has the remedy in its own hands, namely, the purification of its own water supply.

At the present time there is no general pollution of the lake waters worthy of serious consideration and no general pollution problem is likely to arise for many years. The nearest approach to a general problem is at the southerly end of Lake Michigan where Chicago and a number of large cities are relatively near together.

Fearing lest a general pollution problem might arise in this region, and hoping to secure concerted action on the part of the lake cities to protect the quality of the lake water, the Lake Michigan Water Commission was organized in 1908. It is comprised of public health officials, engineers, water analysts and others from the states of Wisconsin, Illinois, Indiana and Ohio, from the lake cities themselves, with representatives also from the U. S. Public Health and Marine Hospital Service. The Commission has held several annual meetings and its papers contributed have been helpful in stimulating the interest in the general problem.

In 1911 a more extended organization known as the Great Lakes International Pure Water Association was projected and a temporary organization formed.

As sources of inspiration and as centres of scientific discussion, such organizations are of real service. But, inasmuch as each problem is a local one, it is difficult to see how concerted action can be or need be brought about. Nor does it appear that inter-state or international arrangements are necessary in order to bring about the needed local reforms. Scientific co-operation is needed much more than legal co-operation or the promulgation of general laws bearing on the subject.

The instances where the sewage of one city affects the water supply of another, as Detroit and Buffalo, or Milwaukee and Cudahy, are in almost every case contained within the limits of a single state. No international problems of water pollution of any great importance are likely to arise in the near future.

Nevertheless the U. S. Government can, through its Public Health Service, perform a useful service by bringing its influence to bear on individual cities, pointing out the dangers and recommending action where needed. Through its impartial position such recommendations carry weight. The power to compel action by the negligent lake cities naturally lies with the state in which the city is located rather than with the federal government.

It is evident from what has been said that some very important scientific studies need to be made to determine the laws that control the currents of the lakes and influence the dispersion of the sewage discharged into them. But it is not necessary to wait for such studies or to await further developments in the art of sewage treatment, as the obvious remedy for the protection of the lake water supplies is filtration of the water, with provision for its disinfection, if necessary. With the art of water purification so fully developed as it is, so thoroughly tested by experience, and proven to be reliable, no lake city can afford not to adopt this safe and sane method of protecting its citizens against the disease and death that lurk in sewage contaminated water supply.

THE PREVENTION OF INDUSTRIAL POISONINGS

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Industrial Hygiene is in its infancy in the United States, but the active and intelligent interest which has been manifested within the last five years gives promise of healthy growth in the future. Three contributions of real merit have already been made here to the subject; Dr. Alice Hamilton's two important monographs on Lead Poisoning, in the Report of the Illinois Commission on Occupational Diseases (1911), and in Bulletin No. 95 of the U. S. Bureau of Labor for July, 1911; Mr. John B. Andrews' valuable report on Phosphorus Poisoning in Bulletin 86 of the U. S. Bureau of Labor for January, 1910; and Mrs. Lindon W. Bates' study of Mercury Poisoning issued as a pamphlet by the Women's Welfare Department of the New York and New Jersey Section of the National Civic Federation (1912). Meanwhile the American Association for Labor Legislation has been carrying on an active campaign. It has held two National Conferences on Industrial Diseases (at Chicago in 1910, and at Atlantic City in 1912), it has appointed a Committee which presented to Congress an important Memorial on Occupational Diseases, it has organized a vigorous local committee in New York and in its various bulletins has presented a valuable series of original contributions and reviews of European practice. The New York Academy of Medicine has actively co-operated in the work of the local branch and recently the New York Section of the American Chemical Society has appointed a strong Committee for the same purpose. The meetings of the Section on Hygiene of the International Congress of Applied Chemistry and of the Section on Industrial Diseases of the International Congress of Hygiene and Demography furnish an unusual opportunity to review and crystallize what has so far been done here on this subject and to take counsel with eminent European visitors who have made so much more progress along these lines.

I do not propose to discuss the effects of industrial poisoning, some of which have been so ably treated at this session, or even to take up in detail the question of the specific poisons themselves, but merely to review some of the fundamental principles of prevention which apply to them in common. The direct death rate from industrial poisons is of course not large. The 1910 census returns for the Registration Area with a population of 53 million and over 800,000 total deaths showed only 126 deaths from lead and 6 more from other industrial poisonings. It is the heavy burden of sickness, often contributing in an important degree to deaths from other causes, which makes the subject so important. The extent of this disease it is now impossible to measure. Reporting of occupational diseases was first required in 1911 in California, Connecticut, Illinois, Michigan, New York, and Wisconsin; and Maryland and New Jersey followed in 1912. These laws are too recent to furnish any basis for judgment as to the extent of industrial disease, but they already show that the relative importance of various poisons is much the same as in Europe, and that lead is by far the most important of them. Thus nine months in Illinois revealed 240 cases of lead poisoning, 6 of arsenic poisoning and 1 of phosphorus poisoning. Dr. Hamilton in her intensive study in the same state found 578 cases of plumbism in a period of three years. The first six months of reporting in New York state showed 87 cases of lead poisoning 2 of arsenic poisoning, 1 of mercury poisoning and 1 of phosphorus poisoning. During the years 1909 and 1910, 60 deaths from lead poisoning were reported in the same state. Mrs. Bates, working as a private investigator and with no official backing, found records of 80 cases of mercury poisoning in New York and New Jersey. Mr. Andrews obtained evidence of over 100 cases of phosphorus poisoning in the match industry of the country. Among the other metals beside lead antimony, arsenic, chromium, copper, manganese, mercury, phosphorus, vanadium, and zinc, and their compounds are all responsible for more or less trade diseases. The most important are mercury and arsenic. The excellent statistics of the Home Office of Great Britain showed in 1911, 1018 cases and 97 deaths from industrial diseases distributed as follows: 932 cases and

35 deaths from lead poisoning; 12 cases and no deaths from mercury poisoning; 10 cases and 1 death from arsenic poisoning, and 64 cases and 11 deaths from anthrax, indicating a similar proportion but much less disease.

A second class of industrial poisons includes the organic compounds such as acetaldehyde, acridine, acrolein, amyl acetate, amyl alcohol, aniline, benzine, benzole, chlorodinitrobenzol, chloronitrobenzol, diazomethane, dimethylsulphate, dinitrobenzol, formaldehyde, methyl alcohol, methylbromide nitraniline, nitro-benzol, nitro-glycerin, nitro-naphthalene, oxalic acid, petroleum, phenol, phenyl-hydrazine, picroc acid, pyridine, tar and turpentine oil. In a third group may conveniently be classed the oxides and other simple compounds of carbon nitrogen and sulphur (carbon monoxide, carbon dioxide, carbon disulphide, carbon oxychloride, the nitrous and cyanogen compounds, hydrogen sulphide, sulphur chloride and sulphur dioxide) many of which are acutely poisonous. Finally, in a fourth group, may be placed the fumes of the halogens, the mineral acids ammonia and chloride of lime, which are more irritant than poisonous but which may produce more or less serious chronic effects upon the mucous membranes. All of the substances mentioned are included in the list of industrial poisons prepared for the International Association for Labor Legislation by Drs. Sommerfeld and Fischer of Germany, Teleky of Austria, Langlois of France, Oliver of England and Devoto of Italy, with the branches of industry in which they are used, the mode of entrance and symptoms of disease, (translated in Bulletin No. 100, U. S. Bureau of Labor, May 1912). Some of them are highly dangerous but used only in small industries. Some do not produce very serious derangements and are included in the official list only to give it approximate completeness. Others like benzine, carbon monoxide, and wood alcohol which produce grave and more or less chronic disturbances of the nervous, respiratory, circulatory, or digestive systems, with a progressive lowering of general tone, are used in a wide range of industries by a large number of workers and are probably in the aggregate more important than any other industrial poisons except lead.

The prevention of industrial poisoning involves in various

cases four different methods of procedure, the elimination of the poisonous substance in favor of a harmless substitute, the handling of the substance in closed vessels or in the wet way and the removal of unavoidable fumes and dust by suction fans, the formulation of rules for the sanitary conduct of dangerous processes by the workman himself, and the detection and treatment of incipient cases of poisoning before they become serious ones. These four procedures call for the service of four different experts, the chemist, the chemical engineer, the sanitarian and the physician.

In the first place it is obvious that the most satisfactory way to deal with industrial poisonings is to do away with the dangerous substance entirely and to replace it by some other non-poisonous material. This is the only way to secure absolute safety. In the case of white phosphorus, attempts were made in the leading European countries to regulate and safeguard the use of the poison but without success. Finally the sesquisulphide substitute was discovered in France and that country prohibited the use of poisonous phosphorus in 1897. Through the efforts of the International Association for Labor Legislation an International Conference was held at Berne, in 1906, which led to similar prohibition in most of the important industrial nations. Great Britain followed suit in 1910. After a vigorous agitation the United States Congress on April 9th passed an Act Providing for a Tax on White Phosphorus Matches and for Prohibiting their Import or Export which will do away with the horrors of phossy jaw after next June. A short time ago I visited a match factory where poisonous and non-poisonous matches were being manufactured side by side; but as we watched a lad at work by the white phosphorus mixing kettle the Superintendent remarked: "He won't get it. We stop making that kind this week."

How far absolute prohibition of other poisonous substances may be practicable is primarily a problem for industrial chemists. In many cases it may undoubtedly be feasible to find cheap and harmless substitutes if attention is seriously turned to the question. In the case of lead paints which unquestionably kill more people than any other industrial poisons, France has boldly taken the bull by the horns, declaring in the law of July 20, 1909, that

"At the end of the fifth year, after promulgation of the present law, the use of white lead, of linseed oil mixed with lead, and of all specialized products containing white lead will be forbidden in all paint, no matter its nature, carried out by working painters either on the outside or on the inside of buildings. A public health order on the advice of the consultative committee of arts and manufactures and of the committee of industrial hygiene shall indicate, if need be, the special kinds of work in which the preceding regulation can be abrogated." Arsenic is to-day voluntarily excluded from many industries where it was once used. Carbon bisulphide has almost ceased to be an industrial danger in rubber making. On the other hand, the English authorities, after exhaustive studies of lead and lead substitutes in the pottery industry, (*Report of the Departmental Committee on the Dangers from Lead, Dust and other Causes in the Manufacture of Earthenware and China, 1910*) could not bring themselves to the prohibition of lead glazes.

The suggestion that leadless glazes should be used in pottery making or that leadless paints should be used for house painting would no doubt meet with strenuous opposition in this country as has been the case in England. Any new suggestion in regard to industry is sure to arouse conservative protests for industry has its full share of the men who have "always done it that way." It is time, however, that the industrial chemist attacked the problem. Let us find out just what would be the cost and the field of usefulness of such harmless substitutes as leadless paints and many of our problems of industrial poisoning will disappear; and they will entirely disappear in no other way. It is significant that in England with an elaborate system of regulation, superior to anything we are likely to attain in this country, there were still 738 cases of lead poisoning and 73 deaths in 1910, and 932 cases and 85 deaths in 1911.

When poisonous substances are the only ones available for industrial purposes at reasonable cost, we must turn to methods of safeguarding them, so far as possible. Since industrial poisoning takes place mainly in two ways, by dust or fumes breathed in from the atmosphere, and by solid particles taken in through the mouth, prevention must follow the two lines of dust and fume

elimination and personal sanitation. On the whole the problem of dust and fumes is probably most important. The acids and halogens, the oxides of carbon and nitrogen, benzine, wood alcohol and most of the organic poisons are taken in as gaseous fumes. Arsenic, copper, lead, mercury, and zinc compounds are also absorbed in the gaseous state, and, to an important degree, in the form of dust. The making and handling of Paris green is one of the most fertile sources of arsenic poisoning as a result of the fine dust produced. The most dangerous of all lead occupations are the handling of lead carbonate in white lead making and the dry scraping of lead paints, as in car and coach painting.

The most satisfactory way to deal with this phase of the problem is to carry on the dangerous processes in closed vessels or in a moist state and in many cases this has been effected with success. In most of the Eastern plants of the National Lead Company the whole process of white lead making is carried on under cover from the point at which the corrossions are dumped into a chute connected with the first cylindrical screen. In the older plants one of the worst processes was the dry grinding, but this is now done in oil, so that there is practically no atmospheric contamination in any of the later stages of the work. There are unquestionably many other dangerous industrial processes where the ingenuity of the chemical engineer could devise similar safeguards if his attention were turned to the matter. One of the most dangerous occupations in lead smelting is that of the men who go in to clean out the bag filter chambers, but similar filters in other factories are cleaned mechanically and under cover. The finishing of paints is in certain cases effected by the use of pumice and oil instead of the deadly dry sandpaper. No one outside the industry can safely dogmatize as to the practicability of new processes of this kind. The industrial chemist may well give them his serious consideration, however, and it seems reasonable that state authorities should enforce the general principle expressed in the recommendation of the Massachusetts State Board of Health in 1907 that there should be required "so far as is reasonably practicable under the varying circumstances, as efficient protection to the health of the operatives in any

occupation as is provided in that occupation where, within the Commonwealth, such protection is most efficient."

Where dust and fumes cannot be entirely suppressed by the use of moist processes or closed vessels, removal by means of hoods and suction fans will minimize the danger. This is especially applicable to many of the processes in which benzine and wood alcohol are used, to pressing irons and other heating appliances likely to produce carbon monoxide, to fur cutting and felt hat making which cause so much mercury poisoning and to the smelting of lead and the handling of white lead and red lead compounds. There are suction systems and suction systems, and some of them are so designed as to be highly efficient. In the careful study made by the British Departmental Committee on Earthenware and China Manufacture an appalling number of practical defects in hoods and ducts and fans in actual operation are recorded. This report and the Two Reports of the Departmental Committees on the Ventilation of Factories and Workshops, contain many excellent suggestions as to better methods of construction and the pottery report recommends a minimum suction velocity of 100 linear feet per minute at the point of origin of the poisonous dust or fumes. Exact details require to be worked out for different processes in different industries, but the problem is in most cases not difficult of solution.

Finally there are certain processes, like the opening up of corrosion beds in white lead works and perhaps certain types of paint scraping and finishing, in which the air cannot be freed from poisonous dusts. Here there is only one possible safeguard, to require the wearing of efficient respirators. There is room for an investigation of respirators of different types in common use in order to determine their relative efficiency with dusts of various kinds. It is probable, however, that the muslin cloth and handkerchiefs so often used do not guarantee proper protection. A real respirator is of course hot and uncomfortable and in this country the employer usually satisfies his conscience by saying, "The men won't wear 'em." In the English laws care is taken to place responsibility on both parties so that there shall be no possibility of shifting it. In the 1903 rules for the earthenware and china industry it is provided among the duties of the employer

that "No person shall be employed in the mixing of unfritted lead compounds, in the preparation or manufacture of fritts, glazes, or colors containing lead without wearing a suitable and efficient respirator, provided and maintained by the employer"; and among the duties of employers, it is specified that every person employed shall, when at work, wear the respirator provided.

Dust and fumes in the air are not by any means the only causes of industrial poisoning. In some cases the poison enters through the skin.

The mineral acids, Acridine, aniline and its compounds, antimony, benzine, benzol, bleaching powder, carbon disulphide, the chromium salts, diazomethane, dimethylsulphate, lead salts, mercury, methyl sulphate, nitrobenzol, nitroglycerin, petroleum, phenol, phenylhydrazine, phosphorus, picric acid, prussic acid, pyridine, tar and turpentine oil may either produce local skin affections or lead to more generalized disease after absorption through the epidermis. Neither of these conditions is at once common and serious in its results, except in the case of the chromium compounds which often produce obstinate and painful ulcers. Of greater practical importance is entrance through the digestive tract in the case of anilin compounds, nitrobenzol phenol and the metallic salts. Antimony, arsenic, copper, lead mercury, phosphorus and zinc are all taken into the system in this way with more or less serious results. At a recent conference on industrial diseases a prominent chemist remarked that "Paints are not made to eat." Neither are human excreta made to eat; yet every case of typhoid fever is due to the swallowing of excreta. The sanitarian knows how fatally easy it is for anything on the fingers to reach the mouth, directly, or by way of food, tobacco and other things which find their way there. With living germs the original dose may of course be much smaller than with mineral poisons. In the case of lead, however, which is a cumulative poison, the repetition of even very small doses may produce the most serious results. The problem of prevention in the case of all these poisons, which enter by the skin or the digestive tract, is essentially a problem of sanitation, and involves many of the same principles which operate in the prevention of infectious disease.

Sanitation involves certain given environmental conditions and also a high degree of care and intelligence on the part of the individual workman. If lead poisoning is to be avoided the worker must wear special clothes in the workroom and leave them behind him when he leaves the factory. He must make it a rule to wash his hands thoroughly with soap and hot water when leaving his work at noon and at night and in the more dangerous processes he should supplement this by frequent shower baths. He must absolutely never put food or tobacco in his mouth in the workroom or with unwashed hands. In the lead industry it is desirable to rinse out the mouth with an alkaline mouth wash on leaving work. The vital resistance must be kept up in every possible way and in particular the workman should never come to the factory without breakfast.

Everyone knows that highly trained experts in bacteriological laboratories often neglect such precautions as these and that hardly a year goes by without some one of them paying the penalty with his life. It cannot be expected therefore that any system of regulation will ensure complete safety among factory operatives. An immense practical improvement has been effected, however, where a serious attempt has been made to come as near as possible to perfection, as for example, at the Pullman car works in Illinois. The employer must provide ample washing facilities with hot water and soap and shower baths where possible, and proper provision should be made for washing on the company's time. There must be lunch rooms, or some adequate places where the men can eat in bad weather outside the workroom. There must be good locker facilities for the storage of street clothes during the day and working clothes at night. In dangerous processes the working clothes themselves and the necessary gloves might well be provided. Workrooms should be well lighted for cleanliness in a dark room is next to impossible. Above all, full instruction should be given to the worker when he enters the occupation as to its dangers and the necessary preventive measures; and his attention should be continually called to them by prominent placards. The success of regulation ultimately depends largely on the attitude of the foreman. If the interest of an intelligent foreman can be aroused

remarkable results may be achieved. If he "has been at the work twenty years and has never been leaded" and thinks "there's no danger if a man keeps health outside" results are likely to be disappointing.

Finally, the last link in the chain of protection which should be thrown about those who must face the risks of industrial poisoning, is medical inspection of the worker. There will always remain a modicum of danger, whatever precautions may be taken, short of eliminating the poison. These should be further minimized by careful selection of the workers so that the constitutionally weak may not be exposed to danger, and by periodic re-examinations to detect indications of latent industrial disease. Such examination sometimes fails of its purpose, but frequently it leads to the detections of poisoning at an early stage when medical treatment and removal from the dangerous process may prevent untoward results.

The prevention of industrial poisonings is no simple matter. It will require thought and time and expense. But in the fine words of old Sir John Simon, that the workers in these trades "have causes of disease indolently left to blight them and their work is an intolerable wrong. To be able to redress that wrong is one of the greatest opportunities for doing good that human institutions can afford." This opportunity, so far as the industrial poisonings is concerned, belongs perhaps more to the chemist than to the worker in any other field.

INTERNATIONAL STANDARDS FOR COLORED FLUIDS AND A SUGGESTED PLAN FOR SUCH STANDARDIZATION

H. V. ARNY

INTRODUCTION

That the color of certain fluids is a distinct factor in pure chemistry is evident from the employment of such colorimetric tests as that of Nessler, and when we turn to applied chemistry, we find that color of liquid products of such esthetic influence to the consumer as to be of vital commercial value to the manufacturer. This is the philosophy of use of coloring agents in pharmacy and furthermore explains the call for uniformity in the tint of natural colored products. So it is that manufacturers of oils, beer and whiskey seek uniformity in color of their products by the use of colorimeters; that is why Professor Felix Ehrlich (*Zeitschrift Ver. Zuckerind* 59 (1909) 746) has advocated international standardization of caramel by use of the definite brown substance, *Saccharan*, which he prepared from sugar. Professor Ehrlich's effort to establish an international standard for caramel is the partial expression of a still broader need of international uniformity of colors, this need being fittingly expressed by Professor Hans Moeller at the International Pharmaceutical Congress of 1910 (*Berichte der Deutschen pharmazeutischen Gesellschaft*, 10 (1910) 358) as follows:

“Ein neues Gebiet, auf dem—meiner Meinung nach—jetzt internationale Regeln festgesetzt werden sollten ist zweifelsohne das der exakten Farbenbestimmungen.”

The subject was brought to the writer in his capacity of member of the Committee on Revision of the National Formulary, there being entrusted to a sub-committee of which he was a member, the problem of standardizing tincture of caramel (*saccharum ustum*) and tincture of cudbear (*Persionis*) which it is

proposed to recognize in the forthcoming edition of that work. It is needless to repeat the numerous and practically fruitless efforts toward standardization already reported by the writer (*American Druggist* 59 (1912) 35) except to say that while some of the plans tried out were satisfactory, each possessed either one of the two insuperable objections of uncertainty of strength or instability of tint. So it was that such standards for cudbear as stained glass, alkaline phenolphthalein solution and solution of commercial orcein and such for caramel as amber glass and carefully prepared burnt sugar solution were abandoned and after experimentation with tintometers, the following simple, accurate and inexpensive method was devised.

SUGGESTED BASIS OF STANDARDIZATION

From the Lovibond tintometer with its blendings of red, yellow and blue glass slides, it was a simple step to the mixing of standard and stable red, yellow and blue solutions and of the chemical solutions adopted, because of stability and comparative ease of standardization were slightly acidulated solutions of cobalt chloride, ferric chloride and cupric sulphate. Since starting the work, examination of the literature has shown that Hazen (*American Chemical Journal* 14 (1892) 300) prepared diluted water-testing solutions from potassium-platinic chloride and cobalt chloride and that Crookes, Odling and Tidy (*Chemical News* 43 (1881) 174) used for similar water testing purposes a ferric chloride-cobalt chloride solution in conjunction with a cupric sulphate solution the two solutions operated in two wedge-shaped flasks. But in both of these plans empiric solutions were employed and for the limited scope of matching color of water samples, whereas in the investigation here recorded standardized volumetric solutions were used and the wide range of hues here exhibited are produced.

OPERATION

For the blending, half normal volumetric solutions based on the atomic weights of 1912 were employed.

Standard Red contains 14.74 gm. cobalt to the liter.

Standard Yellow contains 9.308 gm. ferric iron to the liter.

Standard Blue contains 15.8925 gm. copper to the liter.

Three sets of these standard red, yellow and blue solutions have thus far been prepared. The first set was unacidulated and empirically prepared by dissolving the exact molecular proportion of C.P. crystalline chemicals, ferric alum, cobalt chloride and cupric sulphate in water to a half normal solution; but as the iron solution either alone or in combination with the cobalt or copper solution precipitated after standing a few weeks, slight acidulation was necessary to secure permanent solutions and to aid uniformity, all three colored solutions were subsequently prepared with a fluid consisting of 25 c.c. of 31% hydrochloric acid and 975 c.c. of water; while for the iron solution, ferric chloride was substituted for ferric alum.

While the addition of the small amount of acid did not affect the tint of the cobalt or copper solution, it of course changed materially the color of the ferric solution, and hence the blends of the three solutions. In passing, it might be said that the blending of neutral solutions strongly pointed to the interesting fact that *equal volumes of equimolecular solutions of ferric iron, copper and cobalt give a practically colorless fluid corresponding closely with the "neutral tint" of Lovibond* (Measurement of Light and Color Sensations p. 32.)

As will be noted below, when acid is added to the three solutions, the color preponderance is so affected that the neutral gray tint is found in a blending of red 5, yellow 2, and blue 5; the mixture of equal parts of the three solutions being distinctly yellow.

The other two sets of red, yellow and blue solutions were made strictly half normal as per specifications given below.

Red 59.4965 gm $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ diluted to 1000 c.c. with a mixture of 25 c.c. 31% HCl and 975 c.c. water.

Yellow 45.054 gm. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ diluted to 1000 c. c. with a mixture of 25 c.c. 31% HCl and 975 c.c. water.

Blue 62.43 gm. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ diluted to 1000 c.c. with a mixture of 25 c.c. 31% HCl and 975 c.c. water.

Of course, the original solutions were prepared from larger amounts of the three salts and were then diluted to the above

specified half normal strength with acidulated water; new assays being made after each dilution until exact strength was attained. The iron solution was standardized volumetrically by the potassium iodide-thiosulphate method, while the copper and cobalt solutions were assayed gravimetrically. Analytical data as to these assays will be published later in a more extended report of this line of investigation.

One of these sets of assayed solutions was prepared from Kaulbaum's C.P. "Analyse" copper sulphate; Kaulbaum's C.P. "nickel-frei" cobalt chloride and Merck's "reagent" ferric chloride; while the other set, equally carefully assayed, was prepared from the usual C.P. chemicals as found in stock, the idea being to see if trifling deviations from absolute purity would seriously affect the tint of the mixed solutions. Comparison of products of combinations of these two sets of red, yellow and green fluids and that as "unknowns" showed no deviation save in one isolated case out of the 88 hues tried and this very likely was due to some error on mixing.

THE MIXING

The production of the 88 hues mentioned above from the standard red, yellow and blue solutions was the result of mixing all possible combinations of the three fluids that would lead to a finished volume of 12 c.c. when each fluid was used only in cubic centimeter amounts; that is, when fractional parts of the cubic centimeter were not selected. As a full list of these 88 blendings is given below, we need here only mention that the 88 series of combinations of these fluids to make 12 c.c. was empirically chosen as a convenient number and that it goes without saying that an infinite number of hues are possible, if larger volumes are prepared or fractional parts of the cubic centimeter are used as basis of mixing. It might also be added that in the 88 hues, the combinations of any two of the three colors are included. The result of these 88 blends are exhibited with this and show a range of hues covering the entire spectrum from the red of cobalt chloride solution to the blue of copper sulphate solution. This, of course, eliminates the cardinal reds and crimsons and the

azures and navy blues. A number of the hues, it will be noted, are of a neutral tint, due undoubtedly to the absorption of the light ray by the chemicals, under certain conditions of blending. These "neutrals" will be the subject of further study on physical lines.

For convenience sake, the 88 hues have been classified by eye into the following tentative groupings.

| Red Orange Group | | | Yellow Group | | | Yellow Green Group | | | Blue Green Group | | | Neutral Group Reddish | | |
|--------------------|----|----|--------------|----|----|--------------------|----|----|------------------|----|----|-----------------------|----|----|
| R. | Y. | B. | R. | Y. | B. | R. | Y. | B. | R. | Y. | B. | R. | Y. | B. |
| 11 | 1 | 0 | 5 | 5 | 2 | 2 | 7 | 3 | 0 | 4 | 8 | | | |
| 10 | 2 | 0 | 4 | 7 | 1 | 1 | 9 | 2 | 1 | 2 | 9 | 10 | 1 | 1 |
| 9 | 3 | 0 | 3 | 9 | 0 | 0 | 11 | 1 | 3 | 2 | 7? | 9 | 1 | 2 |
| 9 | 2 | 1 | 4 | 8 | 0 | 2 | 6 | 4 | 3 | 1 | 8? | 8 | 2 | 2 |
| 8 | 4 | 0 | 3 | 8 | 1 | 3 | 5 | 4? | 2 | 1 | 9? | 7 | 2 | 3 |
| 8 | 3 | 1 | 2 | 10 | 0 | 3 | 4 | 5 | 2 | 2 | 8? | 8 | 1 | 3 |
| 7 | 5 | 0 | 1 | 11 | 0 | 3 | 3 | 6 | 1 | 1 | 10 | 7 | 1 | 4 |
| 7 | 4 | 1 | | | | | | | 0 | 1 | 11 | 6 | 1 | 5 |
| Green Yellow Group | | | Green Group | | | Blue Violet Group | | | Yellowish | | | | | |
| 6 | 6 | 0 | | | | | | | R. | Y. | B. | | | |
| 6 | 5 | 1 | R. | Y. | B. | R. | Y. | B. | 6 | 2 | 4 | | | |
| 6 | 4 | 2 | 3 | 7 | 2 | 1 | 8 | 3 | 6 | 3 | 3 | | | |
| 7 | 3 | 2 | 2 | 9 | 1 | 0 | 10 | 2 | 1 | 0 | 11 | 5 | 4 | 3 |
| 5 | 7 | 0 | 1 | 10 | 1 | 2 | 5 | 5? | 2 | 0 | 10 | 4 | 6 | 2 |
| 5 | 6 | 1 | 3 | 6 | 3 | 1 | 7 | 4 | 3 | 0 | 9 | 5 | 3 | 4 |
| | | | 2 | 8 | 2 | 0 | 9 | 3 | 4 | 0 | 8 | 4 | 5 | 3 |
| | | | | | | 0 | 8 | 4 | 5 | 0 | 7 | | | |
| | | | | | | 1 | 6 | 5 | 6 | 0 | 6 | 4 | 4 | 4 |
| | | | | | | 0 | 7 | 5 | 7 | 0 | 5 | 4 | 3 | 5 |
| | | | | | | 1 | 5 | 6 | 8 | 0 | 4 | 4 | 2 | 6 |
| | | | | | | 2 | 4 | 6 | 9 | 0 | 3 | | | |
| | | | | | | 2 | 3 | 7 | 10 | 0 | 2 | 5 | 2 | 5 |
| | | | | | | 0 | 6 | 6 | 11 | 0 | 1 | 5 | 1 | 6 |
| | | | | | | 1 | 4 | 7 | | | | | | |
| | | | | | | 1 | 3 | 8 | | | | 4 | 1 | 7 |
| | | | | | | 0 | 5 | 7 | | | | | | |
| | | | | | | 0 | 3 | 9 | | | | | | |
| | | | | | | 0 | 2 | 10 | | | | | | |

THE R.Y.B. HUES

In this tabulation "R" means $N/2 - CO_2 \cdot 6H_2O$; "Y" means $N/2 - FeCl_3 \cdot 6H_2O$ and "B" means $N/2 - CuSO_4 \cdot 5H_2O$; while in the order from top to bottom of the columns the sequence of the solar spectrum is followed. The interrogation point after some of the blendings means a hue which does not fit satisfactorily into the sequence and which however is not "gray" enough to place among the neutral tints.

USING THE HUES

It will be seen from the foregoing table that the 88 combinations afford an excellent range of tints covering most of those required in pharmacy and commerce. The investigation has not, as yet, sufficiently progressed to report an extended line of color values and in this paper mention will only be made of the matching of the two colors entrusted to the writer by the National Formulary Committee.

Before discussing the individual matchings, it might be well to say that the writer has found that a very satisfactory way to match colored fluids is by use of those oblong flint glass prescription bottles known in American commerce as "Tall Blakes" but Nessler tubes give excellent results and for very accurate work the Rowntree-Garaghty colorimeter is best. Details of this phase of the matter is found in a paper in the *Practical Druggist* 30 (1912) 24.

As to caramel, a typical solution made by carefully carmelizing 1 gm. cane sugar and diluting to 500 c.c. was found by two observers to match exactly the half-normal standard solution "R.Y.B. 4-7-1." As to cudbear, a purified extract (made by percolation of the drug with acetone after previous extraction with chloroform) was dissolved in alcohol containing a trace of ammonia and then diluted with water. The purple tint of this dilution did not match any of the "R.Y.B." samples but when the dilution was faintly acidulated with citric acid, similar tints were obtained; although the acidulated cudbear dilution was a trifle more transparent. Since there was some variation, the

cudbear dilution and the "R.Y.B." hues were submitted to five observers as "unknowns" and the reports of these observers are tabulated below in sequence from darkest to lightest. The "R.Y.B." fluids were the assayed half normal blends, "a" and "b" being the two different samples described above. Two cudbear dilutions 1-50000 were employed; one being distinctly acid (a) and the other just past the neutral point (b), the intention being to see if difference in degree of acidity would make a difference in tint.

Matching Cudbear Dilutions with "R.Y.B." Hues

I and II

| | |
|-------------------------------|--|
| a. "R.Y.B. 9-0-3" | |
| a. "R.Y.B. 10-0-2" | |
| b. "R.Y.B. 10-0-2" | |
| Cudbear dilution 1-50,000 "b" | |
| " " 1-50,000 "a" | |
| " " 1-60,000 | |
| " " 1-75,000 | |

III

| | |
|-------------------------------|--|
| a. "R.Y.B. 9-0-3" | |
| b. "R.Y.B. 10-0-2" | |
| a. "R.Y.B. 10-0-2" | |
| Cudbear dilution 1-50,000 "b" | |
| " " 1-50,000 "a" | |
| " " 1-60,000 | |
| " " 1-75,000 | |

IV

| | |
|----------------------|--|
| a. "R.Y.B. 9-0-3" | |
| Cudbear 1-50,000 "b" | |
| b. "R.Y.B. 10-0-2" | |
| Cudbear 1-50,000 "a" | |
| a. "R.Y.B. 10-0-2" | |
| Cudbear 1-60,000 | |
| " " 1-75,000 | |

X

| | |
|----------------------|--|
| a. "R.Y.B. 9-0-3" | |
| Cudbear 1-50,000 "a" | |
| b. "R.Y.B. 10-0-2" | |
| a. "R.Y.B. 10-0-2" | |
| Cudbear 1-50,000 "b" | |
| " " 1-60,000 | |
| " " 1-75,000 | |

From these five reports, one is justified in reporting that the dilution of 1 to 50,000 of that particular extract of cudbear matched the hue produced by blending 10 volumes of half-normal cobalt solution and 2 volumes half-normal copper solution.

GENERAL REMARKS

From the foregoing paragraphs it will be seen that the writer has adopted a nomenclature for the hues covered by the cobalt-ferric iron-copper blends; "R.Y.B. 10-1-1" meaning that proportion of the three half normal colored fluids. This nomencla-

ture is purely tentative and as further experimentation may show the advisability of using other ionic colors, it might be well, in the beginning to call the above cited combination "Co-Fe-Cu 10-1-1."

Soon after beginning the work, platinic chloride was tried out as the yellow fluid and there was prepared a carefully standardized solution which when based on the quadrivalent platinum cation was exactly fifth normal (9.76 gm Pt. to liter). Blending this with fifth normal solutions of cobalt chloride and of cupric sulphate showed that the platinic chloride had much more color than did the cobalt and copper solutions; a blend of 1 volume of platinum solution and 11 volumes of copper solution giving the normal green that is shown in the cobalt-iron-copper blend, 1-5-6. Perhaps the platinum should be considered as the anion.

The pink manganese solutions (chloride and sulphate) were considered but the prepared half-normal solutions were too light to be of service.

In conclusion, the writer wishes to admit that his plan is still in the experimental stage and in its present state has its limitations. While the demonstrated samples show a fine range of orange, yellow and green tints, it is weak in reds and blues. But in his opinion, the plan is the one by which after more extended work, the color standard problem will be eventually solved, possibly by construction of a red-yellow-blue series of anions.

SUMMARY

1. The need of international standards for colored liquids has been expressed in print by Professors Felix Ehrlich and Hans Moeller; has been demonstrated in daily routine of manufacturers of oils, liquors and pharmaceuticals; and attempts to meet this need are seen in the various colorimetric appliances.
2. Most efforts in this direction are of limited application either through cost of appliances or instability or unreliability of suggested matching agent.
3. The writer's plan is the preparation of half-normal slightly acidulated solutions of (red) cobalt chloride (yellow) ferric chloride and (blue) cupric sulphate and blending these in any proportion desired.

4. Starting with the possible combination of the three colors that would make 12 c.c. when fractional portions of the cubic centimeter are not employed, he has prepared a set of 88 blends, the tints of which, tabulated in the paper, range from the pink of cobalt solution to the blue of copper solution.

5. He suggests a system of color nomenclature based on proportion of the half normal red, yellow and blue solutions employed to make the tint and reports on such "Co-Fe-Cu" factors for caramel and for cudbear dilutions.

UEBER DEN METHYLALCOHOL

K. v. BUCHKA

Die im letzten Winter in Berlin vorgekommenen zahlreichen Erkrankungen und Todesfaelle nach dem Genuss von Methylalcohol haben weit ueber die Grenzen Deutschlands hinaus Aufsehen erregt. Nachdem anfangs andere Ursachen vermutet waren, ergaben die auf Veranlassung der Staatlichen Untersuchungsanstalt fuer Nahrungsmittel angestellten Erhebungen sehr bald mit Gewissheit, dass allein die missbraeuchliche Verwendung des Methylalcohols fuer Trinkzwecke diese Ungluecksfaelle veranlasst hatte. Schon frueher sind in Amerika, in Schweden und in Russland aehnliche Massenvergiftungen unter gleichen Krankheitserscheinungen vorgekommen. Aber man hat ihnen zweifellos in aerztlichen Kreisen nicht immer die genuegende Beachtung geschenkt. Es erscheint dies um so merkwuerdiger als der Methylalcohol in reinem Zustande oder als Holzgeist ausgedehnte Anwendung in den Gewerben wie auch in vielen Staaten zur Denaturierung des Aethylalcohols findet. Allerdings hat man hierbei vielfach auch schon Gesundheitsstoerungen an den Arbeitern wahrgenommen. Aber erst neuere Forschungen namentlich der Ophtalmologen haben unzweifelhaft ergeben, dass diese schaedigenden Wirkungen auf den reinen Methylalcohol zurueckzufuehren sind.

Unter diesen Umstaenden erscheint es geboten, dass man in Zukunft noch mehr als bisher die missbraeuchliche Verwendung des Methylalcohols fuer Trinkzwecke fuer die Herstellung pharmaceutischer und methylalcoholhaltiger Zubereitungen und kosmetischer Mittel zu verhindern sucht. Die Nahrungsmittelgesetzgebung ermoeglicht es schon jetzt, gegen die Verfaelschung von Trinkbranntweinen durch Methylalcohol vorzugehen. Der Verkehr mit pharmaceutischen Zubereitungen wird durch die Pharmakopoeen oder auch wohl durch besondere gesetzliche Verordnungen ueberwacht. Die missbraeuchliche Verwendung des Methylalcohols fuer kosmetische Mittel wird man aber nur

durch besondere gesetzliche Vorschriften hindern koennen, wie dies juengst in Deutschland beschlossen ist.

Bei der Ueberwachung des Verkehrs mit jenen Zubereitungen wird der Analytiker darauf Ruecksicht zu nehmen haben, dass einzelne Rumsorten sehr kleine Mengen von Methylalcohol, jedoch nicht immer, enthalten koennen. Die Anwesenheit von Methylestern in kosmetischen Mitteln, Parfums u.s. verhindert nicht den Nachweis des Methylalcohols.

Dieser Nachweis kann entweder nach dem Verfahren von *Riche und Bardy* geschehen oder man oxydiert die den Methylalcohol enthaltende Traktion zu Formaldehyd und weist diesen durch eine der bekannten Reactionen nach. Vielleicht wird man gut tun, die neuerdings in Vorschlag gebrachten quantitativen Bestimmungsweisen, z.B. die Elementaranalyse der den Methylalcohol enthaltenden Traktion nach *Juckenack* noch weiter auszubilden.

Unaufgeklaert bleibt noch die Ursache der heftigen Giftwirkungen des Methylalcohols. In seiner Oxydation zu Formaldehyd oder zu Ameisensaeure kann der Grund nicht gesucht werden. Denn die physiologischen Wirkungen des Formaldehyd und der Ameisensaeure decken sich nicht mit denen des Methylalcohols. Ebensowenig hat sich die gelegentlich geaeusserte Vermutung bestaetigen lassen, dass vielleicht aus der zunaechst entstandenen Ameisensaeure Kohlenoxyd abgespalten werde, das dann jene Vergiftungen hervorrufe. So bleibt nur die Annahme uebrig, dass man es hier mit einer spezifischen Giftwirkung des Methylalcohols zu tun hat, die noch dadurch verstaeert werden mag, dass der Methylalcohol in einigen Organen vor allem auch im Gehirn angehaeuft wird.

CONTRIBUTION TO THE UNIFICATION OF METHODS OF ANALYSIS OF ESSENTIAL OILS

PAUL JEANCARD AND CONRAD SATIE

In a dissertation prepared in 1910-1911 we endeavored to establish the general principles upon which the data relative to Essential Oils depend. We were engaged upon the preparation of a chapter on Essences in a scientific Pharmacopoeia.

It behooves us now to seek to unify the analytical methods employed for the estimation of Essential Oils in different countries, as much for the use of administrative services as for industrial laboratories. We should esteem ourselves happy if the following pages could serve as a basis for discussion at the coming International Congress of Applied Chemistry about to be held at New York in September next 1912.

1ST: DEFINITION OF ESSENTIAL OILS

The purity of an essential oil depends upon its manufacture, and not upon its applications more or less remote. Is the pure essence required for the perfumer, the pharmacist, or the druggist? We cannot consider several kinds of purity but to obtain data enabling us to specify the character of the different essential oil. An essential oil is characterised in a general manner by the following:—

1. The nature of the vegetable matter treated.
 2. The method of extraction employed.
 3. The physical and chemical constants of the product obtained.
- We will now examine in detail these three questions.

(A) *The Vegetable Matter Treated*

It is important to state very clearly the plant treated. This will be determined by the botanical particulars relative to the family, genus, species. Particulars as to the place of culture, season of flowering etc., are indispensable. It is equally import-

ant to specify the part of the plant tested, flowers, flowering sprays, wood, bark etc.

Thus, in the case of Canella, one may have a great number of different essences, according as the Canella of China, Ceylon, or the Seychelles were being operated upon. There would also be differences in the essence from the same Canellas if one distilled the bark, leaves, buds etc. It is equally necessary to state whether the matter were fresh or dry.

(B) Processes of Extraction

Different products are obtained according to the method of extraction employed. Thus, for an essence obtained by steam distillation one must consider a number of points.

- (a) Distillation of the matter with two to four parts of water and steaming in a double-bottomed still.
- (b) Distilling the matter without water in the still, and bubbling the steam through it.
- (c) A combination of processes a and b.
- (d) Distilling under a pressure varying from one to five kilos or distilling under reduced pressure.
- (e) Agitating or not the mass during distillation.
- (f) Using columns of certain dimensions and varied forms to obtain a series of fractions.
- (g) Separating or returning to the still the distilled waters deprived of essential oil.

It would be quite easy to extend this list of modifications into which steam distillation can be divided. One must take account of the quality of the water employed in charging the still, the rapidity of distillation. Each of the above modifications introduces differences more or less important in the composition of the products obtained.

To take a case in point. Suppose one applies modifications f. & g. to the distillation of orange blossoms. In the one case we get Neroli Oil and Orange Flower Water. In the other case Essence of Neroli only. In the first case the essence will only contain a part, about three quarters, of the odorous constituents of the orange flower, in the second case practically the whole.

If now in these two cases one brings into use modification d., one will obtain products more or less rich in esters. Thus then from the same flowers, distilled on the same day, in the same locality, using the same apparatus, but with different methods, one can obtain four essences of Neroli, presenting among themselves differences more or less considerable.

The processes of extraction by steam distillation are not the only methods employed. One may extract essential oils by volatile solvents and then distil by steam or vacuum the products obtained. The volatile solvent can in its turn be replaced by non-volatile solvents, mineral or vegetable oils, fats etc.

(C) *Physico Chemical Constants*

One should be able to identify every product by its organoleptic and its physical and chemical constants. Organoleptic properties are not susceptible to measurement, and therefore are only vague. The odour of a product is a matter of experience, that is to say it is impossible exactly to define the odour of an essence. One can speak of the camphoraceous odour of Rosemary, the aromatic odour of Eucalyptus, and the soft, sweet odour of the Rose. These qualifications, more or less vague and literary, add nothing of importance to one's conception of Rosemary, Eucalyptus, and Rose.

The colour of a great number of essences varies very rapidly with time on account of the action brought about more or less by air and light. Essence of Absinthe is dark green, enabling it to be distinguished at a distance, but if litre bottles are filled with Essence of Lavender, Rosemary, Spike Lavender, Sage, Anise, and Eucalyptus, it will be impossible to classify them by colour alone. The colour therefore is of no importance in the description of an essential oil, especially as one can get the same essences absolutely colourless.

We see then that physico-chemical constants only are the characteristics enabling us to identify essential oils. It behooves us then to be very precise in establishing these constants.

Essential Oils are mixtures of bodies of more or less complex nature possessing different chemical constitution. Pure, well de-

fined bodies have fixed constants; they are mixtures blended by nature. The constants of essential oils vary with the exterior conditions existing at the formation of the essences in the plant, climate, exposure, nature of the soil, method of cultivation, etc. But these constants vary for each essence between certain limits. We propose to specify "general limits," those given by the extreme figures found for each constant. To the description "general limits" we added in 1909 those of "annual limits." It is evident that these last are more narrow than the first. Thus "general limits" permit one to identify an essential oil, and "annual limits" to pronounce as to the purity of commercial products.

An essential oil will then be described by naming the plant treated, the process of extraction applied, and the physico-chemical constants. We will give the two following examples:—

1. *Hyssop*: An essential oil obtained by steam distillation of the flowering stems of *Hyssopus officinalis*—(*Labiatæ*) a perennial plant flowering from July to September. It is cultivated in France (Provence). The yield of essence is from 0.3 to 1 percent. Then one would add the table of physical constants.

2. *Thyme*: An essential oil obtained by steam distillation from the flowering stems of *Thymus vulgaris* (*Labiatæ*) a perennial plant found in France (Provence and Languedoc), Spain, Tunis and Algeria. By steam distillation of the entire plant the yield of essence is from 0.5 to 1 percent. The phenol content depends upon the place of cultivation. The white essences are obtained by rectification.

2ND: DETERMINATION OF PHYSICO-CHEMICAL CONSTANTS

(A) *Physical Constants*

The first question to be settled in determining these constants is the temperature at which the determination should be made. The temperatures proposed are 15°, 20°, and 25°. Each one of these temperatures has its advantages and disadvantages.

The temperature of 15° has been adopted in the 19th century for the determination of certain important measurements. Thus the whole system of alcoholmetry is based upon determinations

made at a temperature of 15°. The disadvantages are that it does not permit the determination of constants of such oils as Anise, Rose etc. One might say that the temperature of 50° should be taken as a basis, because concrete Oil of Orris melts at about 45°.

The temperature of 25° is rather too high as it favours evaporation. It would be a pity to make it official and if the majority of chemists are opposed to a temperature of 15° it would be better to adopt that of 20°.

The principal physical constants to be determined are: the specific gravity; the rotatory power, and the solubility in diluted alcohol. For certain essences it is convenient also to take the congealing point, and in certain instances the melting point.

The secondary constants are the refractive index and the viscosity.

1st. Specific Gravity: The specific gravity is the relation of the weight of a definite volume of essence at 15° (or 20°) to the weight of the same volume of water at 15° (or 20°). This definition may be considered sufficiently accurate for commercial determinations.

This is done by means of a Westphal Aerothermic Balance if one has sufficient of the product, or by means of a Regnault Picnometer, if one has not sufficient.

The chief point to be settled is the following:—Should the determination of specific gravity be made at 15° (or 20°) or should one determine it at some temperature between 10° and 30° and use a coefficient to correct the number found to what it should be if determined at 15° (or 20°)? In the latter case, should we adopt a standard factor applicable to all essences, or a special factor for each one?

We are of opinion that for the facility of commercial work it would be preferable to use a standard factor, which would be 0.0007 or 0.0008.

2nd. Rotatory Power: All the results are understood to apply to a length of 100 mm. at a temperature between 10° and 30°.

For the oils of Lemon and Portugal it is convenient to note the temperature exactly and to use a factor to bring the figure into comparison with determinations made at 20°.

3rd. Solubility: We strongly urge the suppression once and for all of the use of records of solubilities of essences made in Carbon Bisulphide, Chloroform, Carbon Tetra-chloride etc., which are absolutely useless.

Solubility is determined in the following manner. Fill a burette graduated in 10ths of a Cc., with diluted alcohol, put into a test tube 1 Cc. of essence measured with a pipette divided in 10ths of a Cc. Run in the alcohol drop by drop, shaking constantly, and note the temperature of the mixture at the moment of solution.

A solution having been obtained, add alcohol drop by drop with constant shaking up to 20 Cc. and make sure that there is neither deposit nor turbidity. The degree of the alcohol is indicated by volume, that is to say so many Cc. of pure alcohol in 100 Cc. at 15°.

For each essence the solubility is determined in three degrees of alcohol strength varying by 5°. Thus for Spike Lavender solubility is stated in alcohol of 70, 65, and 60 percent.

For certain essences the solubility point is not easy to read. Thus, a great number of essences of Rosemary are soluble one in ten volumes of 80 percent. alcohol, but others equally pure are soluble in this proportion and do not show complete solubility in from 10 to 20 volumes of 80 percent. alcohol. These last essences would be considered soluble by certain chemists and not entirely so by others. In such a case as this it is not a question of actual measurement but of personal opinion.

In our analytical researches upon Rosemary we have endeavoured to replace these vague data by figures more precise and most critical observations as to solubility.

It is equally of interest to settle clearly the method of formulating the results of similar determinations. One essence of Geranium for example dissolves in 2.5 volumes of 70 percent. alcohol. We add an excess of alcohol; a cloudy solution forms with five to 20 volumes of alchool. At the end of a certain time this turbidity becomes modified and solid particles appear. These formations depend upon the temperature of the laboratory, of that of the alcohol, the time taken etc. It is essential to be precise upon all these points.

4th. Melting and Congealing Points: The congealing points of Aniseed Oil and Rose Oil are not determined in the same manner. Thus in the case of Rose Oil the temperature at which the first crystals appear is noted.

5th. Refractive Indices and Viscosity: These constants are in relation with the chemical function for pure essences. In spite of the interest presented by these constants it would be perhaps premature to regulate their determination.

B. Chemical Constants

Organic chemistry, we wrote in 1909, possesses no actual analytical methods permitting of quantitatively separating according to their chemical functions the different bodies of a mixture. This separation can only be approximate, and the accuracy of the figures found depends upon the quantities worked upon. One can only determine figures which are proportionate to the chemical functions. But the determination of these various numbers is sometimes incompatible as amongst themselves. Thus in determining the saponification number the aldehydes are destroyed and the ester number is falsified.

One determines thus, acid and saponification numbers, before acetylation, after acetylation, formylation etc., but it is inaccurate to speak of the content of Acetate of Linalyl, Geraniol, Citral etc. Further, it is essential for each of these determinations to state the accuracy to which a figure may be guaranteed.

For the determination of these figures volumetric solutions are used. We describe as "normal" solutions containing per litre a number of grammes equal to the molecular weight. We think it preferable to speak of molecular weights and not of equivalents per litre. Besides, this is the definition of normal solutions used in physical chemistry.

1st. Acid Number: This is the number of milligrammes of potash necessary to neutralise one gramme of essence. It is determined in the following manner:—Two grammes of essence are weighed into a 100 Cc. Bohemian glass flask, 10 Cc. of 96 percent. alcohol is added and a few drops of phenolphthalein. Titrate with $\frac{N}{10}$ alcoholic potash.

2nd. Saponification Number: This is the number of milligrammes of potash necessary to saponify one gramme of essence. This number is proportionate to the ester content and therefore to that of the alcohols. The determination is made thus:—Weigh two grammes of essence into a 100 Cc. flask of Bohemian glass, add 10 or 20 Cc. of $\frac{5}{2}$ alcoholic potash. Boil on a water bath, using as a reflux condenser a tube 10 to 12 mm. in diameter and 1 metre long. (The time of ebullition is from half an hour for the greater number of the esters to two hours for Terpinyl Acetate. It is then preferable to make two experiments, one of half an hour and another of two hours.) After cooling dilute with water and titrate the excess of alkali with $\frac{5}{8}$ sulphuric acid, using phenolphthalein.

3rd. Saponification number after acetylation: This figure is proportionate to the total alcohol content. It is determined in the following manner:—Boil on a sand-bath for an hour 10 Cc. of the essence with 10 Cc. acetic anhydride and 1 gramme anhydrous acetate of soda. Determine the saponification number on two grammes as described above.

In this determination the tertiary alcohols are partially dehydrated; therefore it is essential always to work under identical conditions.

Under the action of the acetic anhydride, citronellol is transformed into a cyclic alcoholic acetate, iso-pulegol. This aldehyde is reckoned as alcohol.

4th. Saponification number after Formylation: This figure is proportionate to the content of citronellol (Rhodinol) benzylic and phenylic alcohols etc. It is determined thus:—Mix 10 Cc. of the oil and 20 Cc. of Formic Acid 100 per cent.; boil on a sand-bath 3 hours; wash with water until neutral, and determine the saponification number on 2 grammes of the dry product.

It is believed that geraniol treated with formic acid in the presence of tolene is esterified to a considerable degree—at least 80 percent.

5th. Products soluble in Soda: The figure found indicates the phenol content. It is thus determined:—Put 10 Cc. of essence into a 100 Cc. flask with a neck divided into 10ths of a Cc. Add about 50 Cc. of soda solution 5 percent. Shake briskly and fill

up the flask with the alkaline solution to float the undissolved globules into the graduated portion of the neck. After complete separation read off the portion undissolved.

Acids and bodies soluble in water are reckoned as phenol by the above method. To avoid errors it is well to make a second assay exactly as above but replacing the caustic soda solution by a 5 percent. carbonate of soda solution. The phenol content is the difference between the two results found.

6th. Aldehyde and Ketone values: There is no other method known of estimating the aldehydes, inaccurate as it is. The Bisulphite and Sulphite methods are imperfect and irregular. We use the following method:—Boil 1 gramme of the essence for 1 hour on a sand bath; for an essence containing 50–80 percent. aldehyde with a volumetric solution of phenyl hydrazine hydrochloride. Filter, make up to a definite volume with water, and titrate with iodine. This method, though far from perfect, gives comparable results.

GENERAL REMARKS

The estimation of an essential oil depends upon the determination of physico-chemical constants. It is essential that these determinations should be made in the laboratories all over the world by identical methods. Figures found are only of value when obtained under these conditions, and each worker should understand with what degree of accuracy they have been obtained.

We have insisted in the above pages on the general methods employed in the analysis of essences obtained by steam distillation.

The study of methods applicable to the estimation of other odiferous bodies will form the subject of a second article. We have sought to limit the problem of the analysis of essential oils in such a way that each one may have clear ideas upon the questions specially propounded. We have purposely insisted upon the definition of Essential Oils, for our personal experience has shown us that the great divergence of opinion that prevails in drawing conclusions from an analysis shows what confused ideas are prevalent as to what the term "Essential Oil" ought to mean.

UNIFICATION OF PROCESSES FOR COMMERCIAL ANALYSIS AND VALUATION OF ESSENTIAL OILS

JOHN C. UMLEY AND E. J. PARRY

As announced in the Perfumery & Essential Oil Record for March 1912, we have had the very greatest pleasure in conferring with Mons. Jeancard regarding the standardisation or unification of analytical methods as applied to essential oils and perfumery products. In the paper which precedes this, by Messrs. Jeancard and Satie, observations based upon a very wide manufacturing experience are cited. It is our intention to confine ourselves to the subject simply from an analytical standpoint, leaving our honoured friends to deal not only with the analytical side of the question, but also with the manufacturing side, with which in many instances they have special experience.

We should like to state by way of introduction that our attention was first directed to the difficulties of the subject by the discrepancies in the results obtained by different analysts in the examination of essential oils, in fact we think we are justified in revealing that it was in consequence of discrepancies between our own results that we were first led to compare notes regarding the processes and details of processes which are of such great importance.

The discrepancies naturally are not wide, but they may be of commercial importance, and not infrequently the discrepancies may be misunderstood and misinterpreted. We therefore have set ourselves to the task of considering how far it is possible to put forward processes for the analytical examination of essential oils which shall fulfil the object of (1) determining purity; (2) valuation; without having certain important drawbacks. The drawbacks to which we would refer are those which we have already referred to in the Perfumery & Essential Oil Record of December 1911, page 272, namely:—

1. That the analyst should not be made into a machine.
2. That the necessary variations in composition, due to climatic and other conditions, should not be overlooked.
3. That the tests put forward should not be of such limited character as to act as a guide to those whose intelligence is so mis-applied in the preparation of sophisticants.

For the determination of the physical constants of most of the essential oils we take it that there is practical agreement. This applies to the determination of specific gravity, refractive index, and to acidity, and we certainly see no necessity to depart from the conditions, which have been arrived at after mature deliberation, and which are printed in the "Analyst" of November 1911, page 538, and are reproduced in the "Perfumery & Essential Oil Record," December 1911, page 272. The following particulars may be briefly cited:—

Density: Density is the ratio of the mass of a given volume of a body to the mass of the same volume of distilled water at 4° and under normal pressure.

Since the majority of existing tables contain the values at 15° compared with water at 15°, densities are in practice referred to those conditions (alcoholic solutions, and especially solutions of various acids, oils and essences).

An exception is made in the case of solid fats, but the temperature T at which their density has been taken, and also the temperature T of the water to which the density is referred, are to be stated as follows:—

100°/15°, 40°/40°, etc.

Densities are not to be given in arbitrary units (Baume, Tessa, Cartier etc.).

The alcohol content of alcoholic liquids must be given in grammes of alcohol, either per litre or per 100 Cc., and at the same time in volumes of alcohol according to the method in vogue in the particular country, but preferably in volumes of absolute alcohol contained in 100 volumes of the liquid analysed.

Refractive Index: Refractometric measurements are to be expressed as refractive indices with reference to air, for the spectrum line D, and at a temperature of 25°, but at a temperature of 40° for fats.

When, however, it is impossible to work at the temperatures of 25° or 40° as mentioned above, the refractive index may be taken at another temperature T, but this must be designated by the expression "refractive index (T)."

Polarimetric Results: Polarimetric readings are to be expressed in terms of degrees of arc, with centesimal fractions, for a tube of 10 cm., at a temperature of 20° , and for yellow light (D). (N.B. For essential oil analysis, polarimetric results are best determined in a tube of 100 mm.)

We would however like to make the following qualification in speaking of the standardisation of methods in reference to physical constants in essential oils. The question of determination of these constants at given temperatures is merely a matter of convenience, and we should only suggest that they should be accepted as a general guide, so that the reports of various analysts might always be understood when read by other analysts. For example, it would be futile to attempt to bind any analyst in any given country to adhere to a given temperature for these constants, especially when the U. S. P. for example adopts 25 degrees as the temperature for sp. gr. determination, whilst the B. P. adopts 15 degrees.

We would therefore suggest that it be definitely understood that these physical constants are always taken to refer to the temperatures quoted below unless any other temperature is specifically stated in the analyst's report.

It is however after dealing with the determination of the physical constants that many points occur which may lead to misunderstanding between those dealing with essential oil analysis. It is therefore in connection with the examination of essential oils which have considerable commercial importance that we put forward the following general suggestions, not with any idea of finality, but with the view of eliciting criticism of our contribution to this subject, just as our French Friends have done on their side.

We would certainly deprecate the standardisation of analytical methods for the determination of given substances which are really determinable by various well known methods. In the case of such substances as essential oils however the majority of

the determinations in fact relate not to one body but to groups of bodies, which cannot be accurately determined, but which for purposes of convenience are referred to in terms of a given constituent. For example, the esters in bergamot oil are not entirely composed of linalyl acetate, but for convenience, owing to the impossibility of their separation they are always returned as linalyl acetate. The same is true also with oleic acid in olive oil and so on, and since the determination of these groups of bodies is not an exact one, but varies with variability in conditions, we think that standardisation of these processes becomes absolutely necessary.

We propose briefly then to refer to the methods which we have used, in common we believe with the majority of British analysts, for the examination and valuation of the following essential oils:—

(1). (OILS CONTAINING ALDEHYDES, OTHER THAN LEMON OIL)

For the determination of aldehydes in such oils as Cassia, Cinnamon and Lemongrass custom has now so firmly established the use of acid sulphite of soda in preference to the neutral that we think it would be most unwise, if not almost impossible, to attempt to replace the acid by the neutral sulphite. It is true that in the case of Lemongrass Oil the acid sulphite gives a result of about 4 percent. higher than when the neutral sulphite is used, but it is probable that this 4 percent. consists of bodies of an aldehydic nature which in condensation reactions with violet perfumes are manufactured from the oil, so that the measure of the value of the oil to the ionone manufacturer is probably more correct when determined by the acid sulphite than by the neutral salt.

In practice, we think that 10 Cc. of the oil should be used with about 150 Cc. of 30 percent. solution of the bi-sulphite. The reaction proceeds better if the oil is first introduced into the flask, which has stood in the water bath for a minute in order to heat it, and about 75 Cc. of the acid sulphite solution added whilst hot. In the case of Lemongrass Oil, the time of absorption should be one hour, but in the case of Cassia Oil the absorption must go on until every particle of solid matter is

broken down. The flask should be well shaken at intervals of five minutes.

(2). (LEMON OIL)

We think that most analysts who have had considerable experience in the determination of citral will agree that the method of Walther as modified by Bennett gives the most accurate results possible. The exact details of this method are as follows:—

20 grammes of the oil is accurately weighed into a 200 Cc. flask, 20 Cc. of seminormal solution of hydroxylamine hydrochloride in 80 percent. alcohol is added, then 8 Cc. of normal alcoholic potash and 20 Cc. of alcohol. The mixture is boiled for 30 minutes under a reflux condenser, cooled, and diluted with 250 Cc. of water. The hydrochloric acid which remains combined with the hydroxylamine is neutralised with alcoholic potash phenolphthalein being used as an indicator. The hydroxylamine which has not combined with the citral is then titrated with seminormal sulphuric acid, using methyl orange as indicator.

A blank test is carried out without the Oil of Lemon, and the difference between the amount of sulphuric acid required in the two tests represents the amount of hydroxylamine combined with the citral. This figure multiplied by 0.076 gives the amount of citral in the quantity of oil taken.

The only precautions we would draw attention to as being necessary are that the reaction flask should be ground on to the reflux condenser to prevent the slightest loss of hydroxylamine, and the flask should be allowed to get quite cold before the condenser is washed down.

(3). (OILS CONTAINING PHENOLS)

The determination of phenols by means of absorption by a solution of caustic potash is probably the most convenient, and is certainly fairly accurate for all practical purposes.

The determination of eugenol is frequently carried out by the benzyl chloride method, but unless so specified we consider that a report stating the eugenol content in oil of cloves or other oils should be understood to refer to the absorption process.

The only point in connection with this arises from the fact that a small proportion of the nonphenolic bodies are absorbed, and probably this depends to some extent upon the concentration of the alkali. Most satisfactory results are obtained by the use of a 5 percent. solution of ordinary stick caustic potash. 10 Cc. of the oil should be used in a flask of about 150 Cc. capacity. The sp. gr. of the absorbed and unabsorbed portions are not usually taken into account, and we do not think that it would be wise to introduce this correction, since it might vary considerably in different samples of the same type of oil.

(4). (OILS CONTAINING ESTERS)

We think that in the case of oils containing esters one hour should be the accepted time for saponification, unless otherwise stated. The saponification should be carried out with semi-normal alcoholic potash, and no result should be accepted as correct unless after titration it was found that an excess of alkali remained which was at least equal to half that employed. It is useful of course to form two or more saponifications for different periods of time, as indicating the presence of certain artificial esters which are not readily saponified. This is the case especially with terpinyl acetate, and saponification for 30 minutes and for 90 minutes will give strong indications as to the presence or absence of this ester.

The only point arising in regard to the expression of results depends on whether or not the free acids are first determined and the amount of potash necessary to neutralise indicated from the saponification results. In our opinion it is necessary to determine the free acid and subtract the quantity of potash used. This is especially the case in some bergamot oils, where failure to make this correction has led to the oil being returned as containing sometimes fully 1% more ester than it really does.

(5). (OILS CONTAINING FREE ALCOHOLS)

So much has been written of late on the determination of the acetylisable constituents in Citronella Oil that it will only be

necessary to very briefly summarise the acetylation process. We have recently examined a large number of samples, and find that the most concordant results as between different analysts are yielded by the following process:—

10 Cc. of the oil are gently boiled in a reflux condenser with 20 Cc. acetate anhydride, and 3 grammes anhydrous sodium acetate, for two hours. The oil is then washed with brine, such washing being made with brine containing 1 percent. caustic potash. A drop of Phenolphthalein is added to the brine, and if this after shaking with the oil separates in a colourless condition the washing with alkaline brine is repeated. When neutral, the oil is separated, dried by contact with anhydrous sodium sulphate, and from 2 to 3 grammes saponified with semi-normal alcoholic potash for one hour in the usual manner.

(6). (OILS CONTAINING CINEOL)

We do not think that any process which could be suggested for the determination of cineol is sufficiently accurate to allow of its being used as a standard process, and would suggest that there is a good field for work in this direction.

The above suggestions are of course tentative, and if standards for processes of this type should be adopted with official recognition, modifications in various directions would no doubt be suggested, and might form the basis of useful discussion at a later date between essential oil analysts.

INTERNATIONAL COMMISSION ON VARIATIONS IN THE ACTIVITY OF CERTAIN TOXIC DRUGS

PRELIMINARY REPORT BY THE SECRETARIES

PETER MACEWAN, F. C. S., AND GEORGE P. FORRESTER, F. C. S.

At the last meeting of the Congress in London two papers were communicated to the Pharmaceutical Chemistry Section (1) by Peter Wyatt Squire and Charles W. Caines on "The Standardisation of Potent Drugs, and International agreement in regard to them, and (2) by Peter MacEwan and George P. Forrester on "Variations in the Activity of certain Toxic Drugs, with suggestions for an International Inquiry." After these communications had been discussed the section resolved:—

"That this meeting of the Pharmaceutical Chemistry Section of the International Congress of Applied Chemistry, having received and discussed communications by Messrs. Squire and Caines and MacEwan and Forrester, resolves that it is desirable that an international inquiry should be instituted with a view to securing: (1) greater uniformity in the commercial supplies of potent drugs and the means for determining the same, and (2) approximation in the Pharmacopoeias of the world to common standards of activity.

"With a view to advancing these objects this meeting further recommends that the following Provisional Committee be appointed to inquire and report on the subject to the next meeting of the Congress: Messrs. P. W. Squire and F. Ranson (Great Britain), Professors H. Thoms and E. Schmidt (Germany), Professor E. Bourquelot and M. Léger (France), Professors Piutti and Guareschi (Italy), Professors Remington and Rusby (United States), with Peter MacEwan (Great Britain and U. S. A.) and G. P. Forrester (European Continent) as secretaries.

"This meeting recommends that the Provincial Committee shall have power to invite as members with equal rights persons who have interested themselves in this subject, and further that this resolution shall be conveyed to the Governments and Phar-

macopoeial authorities who were represented at the Brussels Conference (1902) on the unification of potent remedies."

This resolution was confirmed at the final general session of the Congress on June 2, 1909, but it appears not to have been communicated to the respective governments of those countries which have national pharmacopoeias, and if it be desired to continue the inquiry on an international basis some effort might be made to repair the omission.

In their paper three years ago the Secretaries remarked that "a central bureau etc. might be nominated or selected for the purpose of co-ordinating the facts, and to serve as an exchange for all correspondence among the members, especially to facilitate intercourse in the different languages. When all the views have been collected and prepared, the committee should consider them, publish if thought desirable with the view to getting further advice on the proposed methods, and when that question is finally settled the real research work should begin."

The Secretaries have endeavoured to do their part of this proposal, but it soon became apparent that the standardisation of methods for evaluating the activity of the toxic drugs is of secondary importance to their supply. The bulk of the world's supplies of aconite, belladonna, digitalis and henbane come from central Europe, and are gathered from wild plants. This industry, if it may so be called, is of a fortuitous character, and ultimately depends upon labour conditions, so that when the belladonna is just right for collection the gatherers may be employed at something that pays them better, and the belladonna has to wait their pleasure. Meanwhile its alkaloidal value is diminishing. Similar conditions apply to the other toxic drugs, and so far as cultivation is concerned the secretaries have ascertained that farmers on the continent of Europe who make drug cultivation a business, are abandoning these toxic plants in favor of herbs of a culinary nature, which pay them better, first because there is a better market for them and they need less attention. For these and other circumstances it appears to the secretaries that variation in the activity of the toxic drugs referred to is a phase of the larger problem of supply that attends, more or less, the provision of all drugs, the growth of which man is content to

leave to nature, he simply cultivating according to his wants with little regard to the future, and smaller respect to quality. The experience of the United States Bureau of Plant Industry as regards American drugs is an example of these statements, which, however, are based upon more fortuitous circumstances of European collection. The Secretaries are pleased to report that the need for attention to the question of better supply of the toxic drugs is being recognised in Europe and America. Work has been started independently in America, Austria, England, France and Sweden with the view to studying the best conditions upon which the toxic drugs can be cultivated and harvested, so that supplies may be ensured of drugs of pharmacopoeial quality in quantity sufficient for the demand. This is specially true of belladonna and Mr. Francis Ransom, a member of the British Committee, had devoted a portion of his firm's herb farm to the cultivation of *Atropa Belladonna* on an experimental scale and systematic manner, so far as conditions and manurial influences are concerned, in a district where medicinal herbs have been grown for generations, and he has supplemented the accumulated experience of his firm in herb growing with the enthusiasm and science of coadjutors skilled in botany and chemistry. The results of this work are embodied in a separate communication to this section by Francis Ransom and H. John Henderson. They are of a nature which appeals equally to commercially-minded and scientific pharmacists, since they show how cultivation may be altered so that an acre of soil may grow six times more of the plant than it does under natural and unaided conditions, while the alkaloidal value of the drug is also largely increased. It is scarcely possible to discriminate between the importance of the results in these two aspects, but it may be pointed out that Messrs. Ransom and Henderson's data indicate the conditions under which belladonna of different alkaloidal strengths may be grown, and the man who wants the drug for making alkaloid learns the conditions under which a field which has been accustomed to yield him 6 kilograms of atropin will give him 146 kilograms. (Compare A in 1910 with K in June 1911.)

Hitchin is a district not far distant from Rothamsted where in 1840 John Rennet Lawes commenced those agricultural exper-

iments on grass and cereals in which he was joined in 1843 by Joseph Henry Gilbert, and which are still going on in this year of grace 1912. May the same success attend Ransom and Henderson in the experiments which are in their third year.

Similar work to Mr. Ransom's is also being carried on at the herb farms of Messrs. Burroughs Wellcome & Co., near Dartford, Kent, and a communication in regard to the results is being made to this section by Mr. Francis Carr, F. C. S.

Kindred work has been done in France by M. Chevalier at Houdan ("Comptes Rendus," 1910, 150, p. 344) where a field containing 50,000 plants per acre was placed at his disposal. The soil was permeable, contained 3.22 to 4.8 per cent. of lime and 0.07 per cent. of phosphoric acid, and nitrogenous manures equal to from 0.12 to 0.15 per cent. were applied. The principal results obtained were as follows:

| | Alkaloid per cent. |
|--|----------------------------|
| Plants grown in the usual way | 0.320-0.336 |
| Phosphate and potash manures applied | 0.480-0.490 |
| Nitrogenous manures only (1) Biennial plants | 0.616 |
| | (2) Young plants |
| | Rich soil |
| Nitrogenous manures on | 0.406 |
| | Stony soil |
| | Dry soil |
| | 0.676 |
| | 0.680 |
| | 0.756 |

The crops from these plots gave, when used for galenical preparations, an average alkaloidal content of 0.5104 per cent. for the dry leaves. Experiments with *Datura Stramonium* gave quite analogous results, the alkaloidal content of plants manured with nitrogenous products being 0.200 to 0.268, as compared with the normal 0.07 to 0.18.

Experimental work on the cultivation of medicinal plants is also being commenced in Gripholm, Sweden, amongst them being belladonna and henbane. There has been little success so far.

Besides the foregoing, work is being done in the United States on native medicinal plants, as well as on belladonna, digitalis and other plants which yield important drugs, and it appears to the Committee that it will be useful to keep in touch with these various centres of activity in different parts of the world.

(*Abstract*)

METHODS FOR DETERMINING ANTISEPTIC PROPERTIES

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The article treats of the common use of the term antiseptic and also the methods in use for determining antiseptic properties. The methods are outlined, as are also the form of organisms used and the factors considered. In the interpretation of results, from work done by the writer, the suggestion is made that in tests made to determine the antiseptic properties of a substance an organism should be used possessing pronounced powers of adaptation, so that functional disturbances might be readily noted, the bacteria being too minute, and the higher organisms, both plants and animals, being too sluggish to detect any but violent changes. Fungi, other than bacteria, are suggested as test organisms, since they are sufficiently differentiated to show functional disturbances and may be examined microscopically while alive. In the interpretation of antiseptic properties, the quality of the action should be considered so as to differentiate between partial starvation caused by physiological drought, due to excess of a harmless substance, and an actual toxic action. With the organism used by the writer, and with substances diluted to such an extent as to be incapable of affecting the growth as a whole, the characteristic toxicity could be noted by means of the microscope upon the seemingly least resistant parts.

FORTBILDUNGSKURSE FÜR NAHRUNGSMITTEL- CHEMIKER

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Einem jeden, der sich mit der Nahrungsmittelchemie wissenschaftlich beschäftigt, ist es bekannt, welchen Aufschwung dieser Zweig der angewandten Chemie in den letzten Jahrzehnten genommen hat. Die ausserordentliche Entwicklung und Ausgestaltung der Untersuchungsverfahren, die bei der Prüfung der Lebensmittel angewandt werden, hat in verschiedenen Ursachen ihren Grund. Wenn man sich auch in früherer Zeit schon gelegentlich mit Fragen der Nahrungsmittelanalyse beschäftigte, so wurde doch ein Anlass zu zielbewusster und systematischer Durcharbeitung dieses Wissensgebietes erst gegeben, als man in allen Kulturstaaten dazu überging, den Verkehr mit Lebensmitteln gesetzlich zu regeln. In dieser Hinsicht ist für die Mehrzahl der Staaten das letzte Viertel des abgelaufenen Jahrhunderts von besonderer Bedeutung geworden, wenn auch schon früher in einzelnen Staaten mehr oder weniger unfassende Gesetze und Verordnungen auf dem in Frage stehenden Gebiete gegeben waren.

Mit dieser Entwicklung der Nahrungsmittelgesetzgebung fällt zeitlich die weitere Ausgestaltung des Handelsverkehrs, auch in internationaler Beziehung, der allgemeine wirtschaftliche und technische Aufschwung und die Erschliessung vieler Gegenden mit reichen Naturschätzen für den Weltverkehr zusammen.

Es konnte nicht ausbleiben, dass hierdurch zwischen den verschiedenen am Weltverkehr beteiligten Staaten zahlreiche Beziehungen sich ergaben, die früher nicht bestanden und dass vieler Orten neue Erzeugnisse auf dem Nahrungsmittelmarkt auftauchten, die bis dahin noch nicht bekannt waren. Dazu kommt, dass auch altbekannte Rohstoffe durch die Vervollkommenung und Entwicklung der technischen Verarbeitung vielfach in veränderter Form auf dem Markte erschienen.

Wie die Nahrungsmittelgesetzgebung so nahm aber auch die Zoll- und Steuergesetzgebung an dieser neuen Entwicklung des Verkehrs mit Nahrungsmitteln regen Anteil. Wie es die Aufgabe der Nahrungsmittelüberwachung ist, für die Reinhaltung der Lebensmittel in dem durch die Forderungen der Gesundheitslehre bedingten Umfange sowie für Aufrechterhaltung von Treu und Glauben im Handel und Verkehr zu sorgen, so hat überall da, wo staatliche Abgaben in Form von Zöllen oder Steuern auf Nahrungsmittel oder Genussmittel gelegt sind, der Staat auch ein Interesse daran, dass das Aufkommen der gesetzlich festgelegten Abgaben von diesen Waren hinreichend gesichert wird. Auch hierfür ist aber in vielen Fällen eine eingehende chemische Untersuchung erforderlich. Denn häufig richtet sich die Höhe solcher Abgaben nach dem Gehalt der abgabepflichtigen Waren an bestimmten Stoffen, z. B. an Alkohol in weingeisthaltigen Flüssigkeiten; häufig sind auch Vergünstigungen, z. B. Befreiung vom Zoll oder überhaupt die Einfuhr ausländischer Waren an einen bestimmten Reinheitsgrad der betreffenden Waren gebunden (Beispiele: Olivenöl und Wein).

So hat daher der Staat aus verschiedenen Gründen ein sehr reges Interesse daran, dass die Verfahren zur Untersuchung der Nahrungs- und Genussmittel ständig weiter entwickelt und auf der Höhe gehalten werden.

Von nicht minderer Bedeutung aber ist es, dass die chemischen Sachverständigen, welche mit der Untersuchung von Lebensmitteln, gleichviel aus welchem Grunde, beauftragt werden, ihrer Aufgabe gewachsen sind. Dazu gehört neben einer hinreichenden sachlichen Ausbildung eine Summe von Erfahrungen, die natürlich erst mit der Zeit erworben werden kann. Für die erforderliche sachliche Ausbildung zu sorgen, ist die Aufgabe des Staates, bei der Sammlung der Erfahrungen wird schliesslich jeder selbst das Beste tun müssen. Aber trotz dieser selbstverständlichen Pflicht eines jeden Einzelnen wird es doch oft gut sein, wenn auch von dritter Seite etwas dazu geschieht, vorhandene Schwierigkeiten aus dem Wege zu räumen. Und solche Schwierigkeiten stellen sich dem Einzelnen nur zu leicht und aus verschiedenen Gründen entgegen.

Die Entwicklung neuer Untersuchungsverfahren hat zeitweilig

einen etwas schnellen Schritt eingeschlagen. Die fachwissenschaftlichen Arbeiten auf dem Gebiete der Nahrungsmittelchemie schwellen in bedenklicher Weise an. Es wird daher immer schwerer, die Fortschritte der Nahrungsmittelchemie so zu verfolgen, dass man den gesamten Stoff beherrscht.

Dazu kommt, dass auch die Pflichten, deren Erfüllung der Beruf von dem Nahrungsmittelchemiker bei der Ausübung seiner überwachenden Tätigkeit täglich fordert, ständig wachsen. Der Bereich der zu untersuchenden Nahrungsmittel wird immer weiter gezogen. Die Eigenart vieler Nahrungsmittel und die Anforderungen des Handels und Verkehrs verlangen vielfach eine ungesäumte Erledigung der Prüfung. Man denke z. B. an die Überwachung des Verkehrs mit Milch, namentlich in der heissen Jahreszeit, und daran, dass aus dem Auslande in grossen Schiffsladungen eingehende WarenSendungen schon zur Vermeidung hoher Lagerkosten und anderer Unzuträglichkeiten, eine tage lang dauernde Untersuchung nicht vertragen.

So bleibt dem chemischen Sachverständigen neben seinen dringlichen Berufspflichten nicht allzuviel Zeit, sich wissenschaftlich zu betätigen. Vielfach muss er sich auch auf ein bestimmtes eng umgrenztes Gebiet werfen, und gerät dann immer mehr in Gefahr, die Fühlung mit dem gesamten Gebiete zu verlieren. Dieser Gefahr kann nur dadurch begegnet werden, dass dem Nahrungsmittelchemiker durch geeignete Fortbildungskurse von Zeit zu Zeit Gelegenheit gegeben wird, seine Fachkenntnisse aufzufrischen und zu erweitern. Dieser Weg ist neuerdings, und wie es scheint mit gutem Erfolg, in Deutschland beschritten worden. Nach dem Vorbilde anderer Berufsstände, z. B. der Ärzte, der Lehrer, der Verwaltungsbeamten und der Richter wurde Ausgang März dieses Jahres in Berlin ein 14 Tage dauernder Fortbildungskursus für Nahrungsmittelchemiker abgehalten. Der Zweck dieses Kursus wurde durch Vorträge und praktische Übungen angestrebt. Es kann in diesem Augenblick nicht meine Aufgabe sein, hier auf die für den vorliegenden Zweck auch nebensächliche Frage der Organisation einzugehen. Doch will ich erwähnen, dass ausser anderen Fragen vor allem die neueren serologischen Untersuchungsverfahren von Uhlenhuth, ernährungs physiologische Fragen, die Anwendung physikalisch-chemischer

Lehren auf die Nahrungsmittelchemie, ferner Fragen der Weinchemie, die Untersuchung der Fette und des Honigs, sowie Fragen der Gesetzgebung und Rechtsprechung zum Gegenstand der Erörterung gemacht wurden. Die Kurse werden, wenn auch in etwas anderer Weise organisiert, wiederholt werden

Der Umstand, dass auch zahlreiche Ausländer an dem Kursus teilnahmen beweist an sich eigentlich schon, dass eine Frage von internationaler Bedeutung vorliegt. Aber auch aus anderen Gründen muss man schliessen, dass diese Frage ein allgemeineres Interesse beanspruchen darf.

Die Bedürfnisse der Nahrungsmittelchemiker in wissenschaftlicher Hinsicht sind bei der in den Grundzügen gleichen oder einander ähnlichen Gesetzgebung der Kulturstaaten überall gleich. Wo aber einzelne Forscher durch ihre wissenschaftliche Tätigkeit neue Gebiete erschliessen oder wichtige Untersuchungsverfahren ausarbeiten, da hat es zweifellos einen besonderen Wert, wenn diesen Gelehrten Gelegenheit gegeben wird, das Ergebnis ihrer Arbeiten selbst vorzutragen.

Ausserdem ist es auch von grosser Bedeutung, wenn von sachverständiger Seite die oft schwierigen Fragen der Gesetzgebung und Rechtsprechung auch einmal vor einem Kreise von Sachverständigen anderer Nationen besprochen werden, nicht um die Zweckmässigkeit dieser oder jener Bestimmungen zu erörtern, sondern um das Verständnis der hier in Frage stehenden Gesetzgebung und Rechtsprechung in weiteren Kreisen zu fördern. Nur zu oft sind die Bestimmungen der Nahrungsmittelgesetzgebung in anderen Staaten schwer zugänglich und daher unbekannt.

Wie man im Einzelnen solche Fortbildungskurse einrichtet, ob der Staat oder die Standesvertretung wie jetzt in Deutschland oder einzelne Fachgelehrte, wie bei dem Kursus im März d. J. in Berlin die Sache in die Hand nehmen, ist im übrigen gleichgültig und wird sich nach den jeweiligen Verhältnissen richten. Der Zweck meiner Ausführungen wird erreicht sein, wenn durch sie die Anregung gegeben wird, auch an anderen Orten derartige Fortbildungskurse einzurichten, deren Nutzen zunächst den Einzelnen, damit aber auch zugleich der Gesamtheit zu gute kommt. Denn ich brauche hier in einem Kreise von Fachleuten nicht

näher auszuführen, welche Bedeutung gut geschulte und erfahrene Sachverständige für den gesamten Handel und Verkehr haben. Allerdings bin ich der Meinung, dass die Einrichtung solcher Kurse Sache der einzelnen Nationen sein muss. Das schliesst nicht aus, dass man gegebenen Falls hervorragende Sachverständige aus dem Auslande zuzieht. Aus der Art und Weise aber, wie man diese Frage in den einzelnen Staaten angreift, können wir gegenseitig von einander lernen. Und aus diesem Grunde ist ein internationaler Meinungsaustausch auch hier von Wert. Das haben die Ärzte in gleicher Weise empfunden, als sie im Jahre 1909 das "Internationale Komitee für das ärztliche Fortbildungswesen" begründeten. Der Zweck dieses Komitees ist in folgenden Bestimmungen der Satzungen niedergelegt, die in gleicher Weise auch für uns Chemiker eine Bedeutung besitzen dürften.

"Das Internationale Komitee für das ärztliche Fortbildungswesen hat die Aufgabe, auf denjenigen Gebieten der ärztlichen Fortbildung zusammenzuwirken, deren Förderung durch eine solche gemeinsame Tätigkeit zu erwarten ist. Hierin gehören z. B. Erhebungen über die Organisation des ärztlichen Fortbildungswesens in den einzelnen Ländern und Beschreibung der Einrichtungen (insbesondere Institute) für die ärztliche Fortbildung zwecks gegenseitiger Anregung und Belehrung, Informationen über die Beziehungen des akademischen Unterrichts zu der Fortbildung in den einzelnen Ländern, Mitteilungen über die Gelegenheit zur Fortbildung in den einzelnen Ländern, Austausch hervorragender Gelehrter zwecks Belehrung der Ärzte über bestimmte wichtige Neuerungen, Veranstaltung von Konferenzen im Anschluss an die internationalen Ärztekongresse, statistische Arbeiten, die Förderung ärztlicher Studienreisen in fremde Länder usw."

Velleicht können auch wir uns auf einem späteren internationalen Kongress darüber unterhalten, welche Erfahrungen mit den Fortbildungskursen in den verschiedenen Staaten gemacht worden sind.

THE DETERMINATION OF TARTARIC ACID

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INTRODUCTION

The usual method for the determination of tartaric acid is one which depends upon the precipitation and titration of insoluble acid potassium tartrate. This method was first described by Berthelot and Fleurieu in 1865¹ and has since undergone frequent modifications at the hands of various workers. The method proposed by Halenke and Möslinger² is perhaps the most used of these modifications. Although capable of considerable accuracy under proper conditions, it is open to the objections that the reaction between the acid and the precipitate is never complete and the results are often influenced to a considerable degree by other substances present in the solution.

The method of Chapman and Whitteridge³, in which the acid is precipitated as bismuth tartrate and subsequently oxidized with potassium permanganate in acid solution, is not applicable in the presence of citric, malic and oxalic acids.

J. V. Ferentzy⁴ has described a method for the determination of tartaric acid in the presence of malic and succinic acids which is based on the insolubility of basic magnesium tartrate in 50% alcohol. According to L. Gowing-Scopes,⁵ who has studied the method, it is capable of a high degree of accuracy.

E. B. and F. B. Kenrick² have developed a polaroscopic method for the determination of tartaric acid and tartrates depending on the rotation of the acid in the presence of an excess of ammonia

¹ Berthelot's *Chimie Vegetale et Agricole* (1899), 4, 423.

² Zts. Anal. Chem., (1895), 34, 263; Bur. Chem. Bul. 107, rev., p. 86.

³ Analyst (1907), 32, 163.

⁴ Chem. Ztg. (1907), 31, 1118.

⁵ Analyst, (1908), 33, 315.

⁶ J. Am. Chem. Soc. (1902), 24, 928.

while Richardson and Gregory¹ have described a similar method in which advantage is taken of the increase in the optical activity of tartaric acid on treatment with ammonium molybdate.

One of the most recent methods is that of Kling² in which tartaric acid is precipitated in the form of calcium racemate. Warcollier,³ who has applied the method to a number of fruit juices, reports very accurate results.

The fact that under certain conditions uranium salts produce a marked increase in the specific rotation of the dicarboxylic-oxyacids has recently been made the basis of a quantitative method for the determination of 1-malic acid, first by Yoder⁴ and later by Dunbar and Bacon.⁵

As the specific rotation of d-tartaric acid is increased by treatment with uranium salts,⁶ the presence of this acid interferes with the determination of malic acid by the optical method. The present investigation was undertaken for the purpose of devising a method for the determination of tartaric acid which might also be applied to the determination of both malic and tartaric acids in the same solution. The method finally devised for the determination of tartaric acid, while not capable of the accuracy of the malic acid method, is, nevertheless, believed to be of sufficient value to warrant presentation. It will be presented in this paper while the procedure employed for the determination of both acids in the same solution will be described in a second paper.

The possibility of determining d-tartaric acid by means of the increase in rotation produced on treatment with uranium salts has been pointed out by Yoder⁷ who has presented some brief notes on the subject based on his experiments with malic acid. The procedure suggested by Yoder, however, was not found to be capable of successful application and a search was therefore

¹ J. Soc. Chem. Ind. (1903), *22*, 405.

² Bull. Assoc. Chim. de Suc. et Dist., *28*, 893; Compt. Rend., *150*, 616; Ann. fals. (1910), *3*, 239.

³ Ann. fals. (1911), *4*, 485.

⁴ J. Ind. Eng. Chem. (1911), *3*, 563.

⁵ Bur. Chem. Cir. 76; J. Ind. Eng. Chem. (1911), *3*, 826.

⁶ Walden, Berichte Deutsch. Chem. Gesell. (1897), *30* (3), 2889.

⁷ J. Ind. Chem. (1911), *3*, 573.

made for the conditions under which the effect of uranyl acetate on the rotation of solutions of tartaric acid is proportional to the amount of tartaric acid present within a reasonable range of concentration.

EXPERIMENTAL WORK

If treatment with uranyl acetate produces an increased rotation in tartaric acid solutions proportional to their concentration, it should be possible to determine the amount of the acid present in a solution containing other optically active substances not affected by the uranium salt by simply polarizing the solution after treatment with the reagent and multiplying the difference between this reading and that of the solution which has been freed from tartaric acid by a factor determined experimentally.

In the earliest experiments the attempt was made to apply the same method which is used in the determination of malic acid.¹ Solutions of tartaric acid, both before and after neutralization with sodium hydroxid, were treated with powdered uranyl acetate and allowed to stand with frequent shaking. Portions of the solutions were filtered and polarized at intervals. It was found to be impossible under these conditions to obtain solutions of constant rotations. In the more dilute solutions, containing less than 0.5 gram of tartaric acid per 100 cc., the first readings were made one hour after the addition of uranyl acetate and these were the highest obtained. Hourly readings made thereafter showed a slow drop in rotation, an approximately constant reading being obtained only after from one to three days. In the more concentrated solutions of tartaric acid, the time required to attain a maximum rotation increased with the concentration and was also influenced to a marked degree by the frequency with which the mixture was shaken. In the solution containing two grams of tartaric acid per 100 cc., for example, a maximum rotation, +49.0°V., was attained in six and one half hours while in the same series of experiments, the solution containing three grams of acid per 100 cc. required forty-eight hours to reach a maximum, 70.3°V. After reaching a maximum,

¹ Dunbar and Bacon, Bur. Chem. Cir. 76; J. Ind. Eng. Chem. (1911), 3, 826.

a slow fall in rotation was observed in most cases. Several series of tartaric acid solutions, ranging in concentration from .2 to 4.0 grams of acid per 100 cc., were treated in the manner described with similar results.

It was then suggested that the variations in rotation might be due to the action on the uranium-tartaric complex of acetic acid formed by hydrolysis of uranyl acetate. Five grams of sodium acetate were therefore dissolved in the neutralized solutions before diluting to the final concentration. Under this treatment the time required to reach a maximum was not shortened but the tendency of the solution to decrease after reaching a maximum appeared to be somewhat less marked. It was also noticed that the solubility of uranyl acetate in the solution was markedly decreased.

Various attempts were then made to drive the rotation to a maximum in the course of a few hours. Ammonium uranate was substituted for uranyl acetate without result. When solutions of tartaric acid and sodium acetate were treated with uranyl acetate and heated on a steam bath with a reflux condenser, maximum rotations which remained fairly constant were obtained in from one to two hours but in the presence of sugars sufficient caramelization often occurred to ruin the determination. Agitation of the solutions with uranyl acetate in a mechanical shaking device was finally found to produce a maximum change in rotation in a few hours.

Solutions containing the same amount of tartaric acid give a somewhat lower rotation when neutralized before treatment with uranyl acetate than when treated with the reagent without neutralization. Free mineral acids prevent the formation of the uranyl-tartaric complex and acetic acid appears to have a disturbing influence on the rotation. As these acids may be present in a solution under examination, it is always necessary to neutralize the solution before treatment with uranyl acetate. It is desirable to use an acid solution because a larger change in rotation may be obtained. When the neutralized solution is acidified with citric acid, the rotation of the solution is not disturbed.

The most successful method of procedure is as follows:

Render a measured volume of the tartaric acid solution slightly alkaline to litmus paper with sodium hydroxid, dissolve 5 g. of sodium acetate in the solution, reacidify with a strong citric acid solution, adding a slight excess of the acid, and dilute to 100 cc. Treat this solution with powdered uranyl acetate and agitate with a mechanical shaker for three hours. Enough uranyl acetate must be added so that a small amount remains undissolved at the end of the period of shaking. The optical rotation of solutions containing between .2 and 3.0 g. of tartaric acid per 100 cc. when treated in this manner is closely proportional to the amount of tartaric acid present in the solution.

DETERMINATION OF THE FACTOR

A large number of experiments were made to determine the factor to be used in calculating the amount of tartaric acid from the polarization of the solution after treatment with uranyl acetate. Solutions containing known amounts of pure tartaric acid were treated in the manner described above and polarized in 200 mm. tubes using white light. The factor was obtained by dividing the weight in grams per 100 cc. of tartaric acid present by the rotation in degrees Venzke. The results are shown in Table I. The average factor is 0.051 and this has been adopted for use in all calculations.

As has been stated, the concentration of tartaric acid is practically proportional to the rotation of the uranium-tartaric solution in solutions containing between 0.2 and 3.0 grams of the acid per 100 cc., the ratio being 0.051. Beyond this point the ratio gradually increases. This is probably due partly to a normal decrease in specific rotation with rise in concentration and partly to the diluting effect of the solution of uranyl acetate. A 4% solution of tartaric acid is increased approximately 4% in volume after treatment with uranyl acetate. The increased rotation of the uranium-tartaric solution as compared with the rotation of the straight tartaric acid solution is shown graphically by the curves. "A" represents the rise in rotation with concentration in solutions of pure tartaric acid while "B" shows the increase in rotations of the same solutions after treatment with uranyl acetate.

REMOVAL OF TARTARIC ACID

Walden¹ reports (a)^D for a solution containing 0.75 g. of tartaric acid per 100 cc. as approximately +14.7 circular degrees as compared with +303° for the uranium complex. It is evident that when solutions are under examination which contain other optically active substances in addition to tartaric acid, the latter will have a noticeable effect on the original rotation of the solution. It is, therefore, necessary to remove the tartaric acid from the solution in order to determine the rotation due to other optically active substances present. Dry powdered normal lead acetate is quite satisfactory for this purpose.

Uranyl acetate produces a slight effect on the rotation of sugars². In solutions containing a small amount of tartaric acid (under .5%) and a rather large amount of sugars (over 10%), it is necessary, therefore, to treat the original solution with uranyl acetate after precipitating the tartaric acid and removing the excess of lead with anhydrous sodium sulphate.

The solubility of lead tartrate in water at 25° is .0108 g. per 100 cc². Consequently, the amount of tartaric acid remaining in the solution after precipitation with lead acetate is not sufficient to cause any noticeable increase in the rotation of the solution when uranyl acetate is added.

DETAILS OF THE METHOD

1. Measure 85 cc. of the solution under examination into a 100 cc. graduated flask, render the solution slightly alkaline to litmus paper with sodium hydroxid, add five grams of sodium acetate and shake until dissolved. Reacidify the solution to litmus paper with a strong solution of citric acid, adding a slight excess of the acid, cool to room temperature and dilute to 100 cc. Treat about 30 cc. of this solution with powdered uranyl acetate, transfer to a suitable container and shake for three hours with a mechanical shaker. Add enough uranyl acetate so that a small

¹ Bericht (1897), 30, 2890.

² Bur. Chem. Cir. 76, 5; J. Ind. Eng. Chem. (1911), 3, 826.

³ Partheil and Hübner, Arch. der Pharm., 241, 412; Chem. Zentr. (1903), 74, (2), 1026.

amount remains undissolved after three hours shaking. From two to three grams are usually sufficient. If the uranium salt dissolves more must be added. Filter through a folded filter and polarize if possible in a 200 mm. tube. After polarizing, agitate the solution for an hour longer with uranyl acetate and again polarize to determine whether a maximum rotation has been obtained. Calculate the reading in degrees Venzke to the basis of the original solution and designate as (1).

2. Treat about 50 cc. of the original solution with dry powdered normal lead acetate until no further precipitation results; avoid excess of the precipitant. A centrifuge can be used to advantage in settling the precipitate. Filter through a folded filter and test the filtrate with a small crystal of lead acetate to determine whether precipitation is complete. Remove the excess of lead with powdered anhydrous sodium sulphate, filter until clear and polarize in a 200 mm. tube. Designate this reading as (2). If the solution is supposed to contain less than 0.5% of tartaric acid and more than 10% of sugar, treat the tartaric acid free solution with powdered uranyl acetate and shake at intervals for one hour. Filter and polarize. If the reading so obtained is less than (2), it should be used instead of (2) in the final calculation.

3. Polarize at room temperature with white light, taking care that all solutions are polarized at the same temperature. Make at least six readings on each solution and take the average of these. Calculate all readings to the basis of a 200 mm. tube. Multiply the algebraic difference in degrees Venzke between readings (1) and (2) by the factor 0.051. The result will equal the weight of total tartaric acid in grams in 100 cc. of the original solution.

NOTES ON THE METHOD

In this work a standard, Lippich type, triple field saccharimeter was used, the light being furnished by an electric stereopticon bulb placed behind a ground glass plate.

The most favorable concentration of tartaric acid for the determination is between 0.5 and 2.0 gram per 100 cc. Solutions containing as low as 0.2 g. per 100 may be determined with accuracy,

however, when the color of the solution is not such as to make readings uncertain.

After reaching a maximum, the rotation of the uranium-tartaric solution remains constant and solutions may be kept over night before polarizing. They must be kept in a dark place, however, as they are darkened by exposure to daylight.

Very dark colored solutions may often be decolorized by shaking vigorously with two or three drops of bromine and filtering just before polarizing. Either solution, (1) or (2), may be treated in this way without vitiating the results. It is sometimes advantageous in solutions containing large amounts of pectin bodies to precipitate the latter with two or three volumes of alcohol, wash the precipitate with 95% alcohol and concentrate the filtrate to the original volume, following the procedure for the determination of malic acid in fruit juices described by Pratt.¹

In very clear solutions containing large amounts of tartaric acid, difficulty is sometimes experienced in polarizing owing to the blue color developed in one segment of the field. Under these circumstances, it is advisable to dilute the solution.

A few experiments were made to determine the effect of phosphates, iron and aluminum on the results. In the concentrations studied, the presence of iron or phosphates does not appear to affect the accuracy of the results. A solution containing 0.50 g. of tartaric acid and 1 gram of di-sodium phosphate in 100 cc. yielded 0.49 g. of tartaric acid while another containing the same amount of tartaric acid and 1 gram of ferrous sulphate yielded 0.46 g. Only 0.36 g. of tartaric acid was recovered from a solution containing 0.50 g. of the acid and 1 g. of potassium alum in 100 cc.

DISCUSSION OF RESULTS

The results are tabulated in Tables II and III. Table II contains the record of determinations on solutions of tartaric acid with various sugars. The percentages of sugar given in column 2 are only approximate. This explains the variations in rota-

¹ Bur. Chem. Cir. 87.

tion between solutions which are designated as having the same concentration of sugar. The determinations on fruit juices recorded in Table II were made on solutions in which the amounts of added tartaric acid were unknown to the analyst. It will be noted that the results on blackberry juice and in the lower concentrations on raspberry juice vary most widely from the theoretical. This is due to the fact the the color of these solutions is so intense that a considerable error is likely to be introduced in making the polarizations.

Numerous attempts were made to obviate this difficulty in dark colored solutions by precipitating the tartaric acid with lead acetate in the presence of three or four volumes of alcohol, decomposing the precipitate with sulphuric acid or hydrogen sulphid, concentrating the resulting filtrate and determining the tartaric acid in the solution so obtained. The solutions finally obtained, however, were almost as highly colored as the original samples and the results were irregular and unsatisfactory.

SUMMARY

When a solution of tartaric acid or tartrates containing between 0.2 and 3.0 grams of total tartaric acid per 100 cc. is treated under definite conditions with uranyl acetate, its optical rotation is markedly increased and is proportional to the amount of tartaric acid present in the solution.

Under these conditions, each gram of tartaric acid present in 100 cc. of the solution produces a rotation of $+19.6^{\circ}\text{V}$., the ratio of tartaric acid concentration to rotation being 0.051.

Malic acid is the only other common acid which is affected in this way by uranyl acetate. Hence, in the absence of malic acid, tartaric acid may be determined quantitatively by treating its solution, properly prepared, with uranyl acetate, polarizing and multiplying the reading by the factor 0.051.

In the presence of other optically active substances, a portion of the solution must be freed from tartaric acid by precipitation with lead acetate and polarized separately. The algebraic difference between this reading and that obtained on the solution which has been treated with uranyl acetate will give the polarization due to the uranyl tartaric complex.

The most favorable limits of concentration are between 0.5 and 2.0 g. of tartaric acid per 100 cc. A determination may easily be made in four hours, during three of which no treatment except shaking is required.

TABLE I
Determination of the Factor

| Tartaric Acid present — g. per 100 cc. | Polarization in 200 mm. tube °V. | Factor Calculated | Tartaric Acid found using factor 0.051 |
|---|-------------------------------------|----------------------|--|
| 2.50 | +49.6 | 0.050 | 2.53 |
| 2.00 | +37.9 | 0.053 | 1.93 |
| 2.00 | +38.8 | 0.052 | 1.98 |
| 2.00 | +39.0 | 0.051 | 2.00 |
| 1.75 | +35.5 | 0.049 | 1.81 |
| 1.50 | +30.8 | 0.049 | 1.57 |
| 1.50 | +30.0 | 0.050 | 1.53 |
| *1.49 | +29.4 | 0.051 | 1.50 |
| *1.49 | +28.7 | 0.052 | 1.46 |
| 1.00 | +21.1 | 0.047 | 1.08 |
| 1.00 | +20.5 | 0.049 | 1.05 |
| *0.99 | +19.3 | 0.051 | 0.98 |
| *0.99 | +18.6 | 0.053 | 0.95 |
| 0.50 | + 9.9 | 0.050 | 0.50 |
| *0.50 | +10.2 | 0.049 | 0.52 |
| *0.50 | + 9.5 | 0.053 | 0.48 |
| 0.40 | + 8.0 | 0.050 | 0.41 |
| 0.30 | + 5.7 | 0.053 | 0.29 |
| 0.25 | + 4.6 | 0.054 | 0.23 |
| 0.20 | + 3.9 | 0.051 | 0.20 |
| Average Factor | | | 0.051 |

* Determinations by Dr. J. M. Johnson.

TABLE II
*Determination of Tartaric Acid in Sugar Solutions**

| Sugar present | % Sugar present (approx.) | Tartaric Acid added-g. per 100 cc. | Polarization in 200 mm. tubes ** | | Difference between readings | Tartaric acid found - g. per 100 cc. |
|---------------|---------------------------|------------------------------------|---|---|-----------------------------|--------------------------------------|
| | | | After treatment with uranyl acetate - °V. | Solution freed from tartaric Acid - °V. | | |
| Sucrose .. | 25.0 | 0.50 | +103.8 | +93.5 | 9.3 | 0.47 |
| " .. | 25.0 | 0.49 | +102.4 | +93.2 | 9.2 | 0.47 |
| " .. | 25.0 | 0.25 | +98.3 | +94.5 | 3.8 | 0.19 |
| " .. | 12.5 | 0.25 | +52.0 | +47.3 | 4.7 | 0.24 |
| Dextrose.. | 25.0 | 0.50 | +86.2 | +76.5 | 9.7 | 0.49 |
| " .. | 25.0 | 0.49 | +84.7 | +74.1 | 10.6 | 0.54 |
| " .. | 25.0 | 0.49 | +86.5 | +76.1 | 10.4 | 0.53 |
| " .. | 25.0 | 0.25 | +81.2 | +77.3 | 3.9 | 0.20 |
| " .. | 12.5 | 0.25 | +42.8 | +38.2 | 4.5 | 0.23 |
| Lovulose .. | 22.0 | 0.50 | -99.5 | -109.0 | 9.5 | 0.48 |
| " .. | 25.0 | 0.49 | -123.8 | -135.3 | 11.5 | 0.59 |
| " .. | 25.0 | 0.25 | -115.8 | -120.8 | 5.0 | 0.26 |
| " .. | 12.5 | 0.25 | -54.7 | -59.2 | 4.5 | 0.23 |
| Invert.... | 25.0 | 0.98 | -5.4 | -24.6 | 19.2 | 0.98 |
| " | 12.5 | 0.98 | +10.2 | -12.7 | 22.9 | 1.17 |
| " | 25.0 | 0.50 | -11.3 | -17.2 | 5.9 | 0.30 |
| " | 25.0 | 0.50 | -8.9 | -18.7 | 9.8 | 0.50 |
| " | 25.0 | 0.50 | -21.0 | -29.6 | 8.6 | 0.44 |
| " | 10.0 | 0.50 | -0.9 | -11.4 | 10.5 | 0.54 |
| " | 25.0 | 0.49 | -10.6 | -20.0 | 9.4 | 0.48 |
| " | 25.0 | 0.49 | -12.6 | -22.2 | 9.6 | 0.49 |
| " | 12.5 | 0.49 | 0.0 | -10.8 | 1.1 | 0.55 |
| " | 25.0 | 0.25 | -15.5 | -19.2 | 3.7 | 0.19 |
| " | 25.0 | 0.25 | -24.9 | -29.1 | 4.2 | 0.21 |
| " | 25.0 | 0.25 | -16.6 | -21.3 | 4.7 | 0.24 |
| " | 12.5 | 0.25 | -4.0 | -9.0 | 5.0 | 0.26 |
| " | 10.0 | 0.25 | -6.0 | -11.0 | 5.0 | 0.26 |
| " | 7.0 | 0.25 | -1.2 | -6.7 | 5.5 | 0.28 |
| " | 25.0 | 0.13 | -26.6 | -29.1 | 2.5 | 0.13 |
| " | 10.0 | 0.13 | -8.7 | -10.4 | 1.7 | 0.09 |

* Most of the determinations are by Dr. J. M. Johnson, whose assistance is gratefully acknowledged.

** Calculated to original concentration.

TABLE III
Determination of Added Tartaric Acid in Fruit Juices

| Fruit Juice | Tartaric Acid added — g. per 100 cc. | Polarization in 200 mm. tubes * | | Difference between readings | Tartaric acid found — g. per 100 cc. |
|------------------|--|--|--|-----------------------------------|---|
| | | After treat- ment with uranyl ace- tate — °V. | Solution freed from tartaric acid — °V. | | |
| Strawberry | 0.75 | +8.3 | -6.2 | 14.5 | 0.74 |
| | 0.63 | +5.2 | -6.1 | 11.3 | 0.57 |
| | 0.60 | +4.1 | -6.2 | 10.3 | 0.53 |
| | 0.50 | +3.1 | -6.4 | 9.5 | 0.48 |
| | 0.50 | +4.5 | -6.6 | 11.1 | 0.47 |
| | 0.38 | +1.1 | -6.3 | 7.4 | 0.38 |
| | 0.35 | -1.0 | -6.8 | 5.8 | 0.30 |
| | 0.20 | -6.3 | -10.3 | 4.0 | 0.20 |
| Raspberry | 1.00 | +14.5 | -5.0 | 19.5 | 0.99 |
| | 0.75 | +6.3 | -8.4 | 14.7 | 0.75 |
| | 0.70 | +5.3 | -10.1 | 15.4 | 0.79 |
| | 0.50 | +2.1 | -8.0 | 10.1 | 0.52 |
| | 0.40 | -1.1 | -10.4 | 9.3 | 0.47 |
| | 0.25 | -3.1 | -9.6 | 6.5 | 0.33 |
| | 0.13 | -5.0 | -6.6 | 1.6 | 0.08 |
| | | | | | |
| Blackberry | 0.60 | -0.4 | -9.0 | 8.6 | 0.44 |
| | 0.51 | +2.8 | -8.0 | 10.8 | 0.55 |
| | 0.50 | +2.2 | -10.6 | 12.8 | 0.65 |
| | 0.28 | -2.8 | -9.2 | 6.4 | 0.33 |
| | 0.13 | -6.0 | -9.6 | 3.6 | 0.18 |
| | 0.10 | -11.9 | -12.9 | 1.0 | 0.05 |

* Calculated to concentration of the original solution.

Rotation. Degrees Venzke.

60
50
40
30
20
10

Temp. = 20° C

B.

Tartaric Acid + Uranyl Acetate

A.

Tartaric Acid.

1 2 3 4

Tartaric Acid. Grams Per 100 cc.

THE DETERMINATION OF MALIC AND TARTARIC ACIDS IN THE SAME SOLUTION

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INTRODUCTION

The usual method for the determination of tartaric, citric and malic acids in the same solution is a modification of that proposed by Schmidt and Hiepe.¹ It depends on the precipitation of the acids in the form of calcium salts and the separation of these by means of their solubilities in water and alcohol. The separations obtained in this way are far from sharp and the results are usually unsatisfactory.

It is the purpose of the present paper to present some preliminary notes on a new method for the determination of malic and tartaric acids in the same solution. While the work is far from complete, it is hoped that the publication of the results so far obtained may be of some value and may lead to further researches along the same line.

Walden² first pointed out that when malic and tartaric acids are treated with uranium salts under definite conditions marked increases in their optical rotations are produced. Within certain limits these increased rotations are proportional to the concentration of the acids. These facts have recently been used by Yoder,³ Dunbar and Bacon⁴ and Dunbar (see preceding paper) as the bases of quantitative methods for the determination of malic and tartaric acids when occurring separately. Yoder⁵ has suggested that the amounts of these acids present in the same solution may be calculated if some value is determined in addi-

¹ Zts. Anal. Chem., 1882, 21, 534; Bur. Chem. Bul. 107, rev., p. 80.

² Berichte, 1897, 30, (3), 2889.

³ J. Ind. Eng. Chem., 1911, 3, 563.

⁴ J. Ind. Eng. Chem., 1911, 3, 826; Bur. Chem. Cir. 76.

⁵ Loc. cit., 573.

tion to the rotatory power of the solution after treatment with uranyl acetate. He recommends for this purpose the determination of total acidity. It is obvious that this method is only applicable in cases where the only acids present are malic and tartaric and where these are entirely in the free condition.

In the present experiments advantage is taken of the fact that when oxidized with potassium permanganate in the presence of an excess of alkali, malic and tartaric acids, like lactic acid, are both converted quantitatively into oxalic acid. This has been shown by Bacon and Dunbar¹ and has been used by them as the basis of a method for the determination of lactic acid in products made from spoiled tomatoes. When malic or tartaric acids are oxidized in this manner, the oxalic acid which is formed may be determined either by precipitation as calcium oxalate or by titration in acid solution with potassium permanganate. The amount of potassium permanganate reduced may also be determined directly by titration. It is unnecessary to point out that the latter procedure can be employed only in the absence of other reducing substances while the former cannot be used in the presence of other substances forming oxalic acid on oxidation unless it is possible to separate malic and tartaric acids from these substances before oxidation. That the method is capable of determining malic and tartaric acids separately with considerable accuracy is shown in Tables I, II and III.

TABLE I

| Acid. | Wt. of acid present grams. | Calcium oxalate $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ | | Wt. of acid found grams. |
|------------|----------------------------------|---|------------------|--------------------------------|
| | | Found grams. | Theory grams. | |
| Malic..... | 0.25 | 0.530 | 0.545 | 0.243 |
| " * | 0.20 | 0.435 | 0.436 | 0.200 |
| " * | 0.10 | 0.220 | 0.218 | 0.102 |

* Results taken from Bur. Chem. Cir. 78.

¹ Bur. Chem. Cir. 78.

TABLE II

| Acid. | Wt. of malic or tartaric acid present grams. | Wt. of oxalic acid found grams. | Wt. of malic or tartaric acid found grams. |
|---------------------|--|---------------------------------|--|
| Tartaric* | 0.293 | 0.485 | 0.289 |
| " | 0.25 | 0.37 | 0.22 |
| " | 0.25 | 0.41 | 0.24 |
| " | 0.25 | 0.36 | 0.21 |
| Malic | 0.25 | 0.47 | 0.247 |

TABLE III

| Acid. | Wt. of acid present grams. | Wt. premanganate required grams. | Wt. of acid found grams. |
|---------------------|----------------------------|----------------------------------|--------------------------|
| Malic | 0.950 | 2.67 | 0.942 |
| " | 0.498 | 1.39 | 0.493 |
| " * | 0.10 | 0.272 | 0.096 |
| " * | 0.10 | 0.282 | 0.099 |
| " * | 0.10 | 0.301 | 0.106 |
| Tartaric* | 0.10 | 0.211 | 0.100 |
| " | 0.250 | 0.55 | 0.26 |
| " | 0.250 | 0.54 | 0.256 |
| " | 0.250 | 0.54 | 0.256 |

In Table I the oxalic acid formed by the oxidation of malic or tartaric acid was determined gravimetrically, in II it was titrated in acid solution with potassium permanganate, while in III the amount of malic or tartaric acid present was calculated indirectly from the amount of potassium permanganate reduced. In all three tables the results marked with a star (*) are from an earlier paper¹ and are introduced here for the sake of completeness. The details of the methods used will be given later.

* Results taken from Bur. Chem. Cir. 78.

¹ Bacon and Dunbar, Bur. Chem. Cir. 78.

PRINCIPLE OF THE METHOD

As has been stated solutions of both malic and tartaric acids when treated with uranyl acetate under proper conditions show an increased rotation which within certain limits is proportional to the concentration. Both acids also reduce definite amounts of potassium permanganate in alkaline solution and form oxalic acid quantitatively. Hence, it is possible to calculate the amounts of malic and tartaric acids in a solution, knowing the total change in rotation of the solution on treatment with uranyl acetate and also either the amount of potassium permanganate reduced or of oxalic acid formed when the solution is oxidized in alkaline solution.

EFFECT OF URANYL ACETATE ON THE ROTATIONS

It has been shown by Dunbar and Bacon¹ that a solution containing 1 gram of malic acid in 100 cc will rotate -27.77° V. when treated with uranyl acetate under proper conditions. In the preceding paper on the determination of tartaric acid, it has also been shown that a solution containing 1 gram of tartaric acid in 100 cc will when treated with uranyl acetate under proper conditions produce a rotation of $+19.61^{\circ}$ V. In a solution containing both acids, these changes in rotation are produced by each independently of the other.

REACTION OF MALIC AND TARTARIC ACIDS WITH POTASSIUM PERMANGANATE

When malic acid is oxidized with potassium permanganate in the presence of an excess of alkali the following reaction occurs:



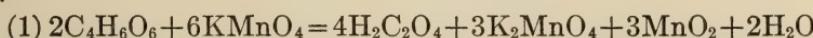
On acidifying this mixture, as is done when the total amount of reduced permanganate is to be determined, oxalic acid is further oxidized by potassium permanganate according to the following equation.:

¹ Bur. Chem. Cir. 76; J. Ind. Eng. Chem., 1911, 3, 826.



One gram of potassium permanganate is equivalent to 0.353 grams of malic acid or 1 gram of malic acid equals 2.8297 grams of potassium permanganate. One gram of oxalic acid, $\text{C}_2\text{H}_2\text{O}_4 + 2\text{H}_2\text{O}$, is equivalent to 0.526 g. of malic acid or 1 gram of malic acid equals 1.90 g. of oxalic acid.

When tartaric acid is oxidized in the same manner the equation is:



On acidifying, the oxalic acid is further oxidized as shown in equation (2) above. One gram of potassium permanganate is equivalent to 0.475 g. of tartaric acid or 1 gram of tartaric acid equals 2.1062 grams of potassium permanganate. One gram of oxalic acid equals 0.595 g. tartaric acid or 1 gram of tartaric acid equals 1.68 grams of oxalic acid.

CALCULATION OF EQUATIONS

Bearing in mind the rotations of uranium-malic and uranium-tartaric solutions containing 1 gram of acid per 100 cc and also the permanganate equivalent to these acids, the equations for calculating the amounts of malic and tartaric acids from the total change in rotation and the amount of potassium permanganate reduced are deduced as follows:

Let x = grams malic acid in 100 cc.

y = grams tartaric acid in 100 cc.

a = polarization in degrees V. of the solution in a 200 mm tube after treatment with uranyl acetate.

b = grams KMnO_4 required to oxidize the acids in 100 cc.

$$\text{Then } -27.77x + 19.61y = a \quad (1)$$

$$\text{and } 2.8297x + 2.1062y = b \quad (2)$$

Solving for x and y , the following equations are obtained:

$$x = -.0185a + .1720b$$

$$y = .0248a + .2436b$$

The equations for calculating the amounts of malic and tartaric

acids from the total change in rotation and the total amount of oxalic acid formed are deduced as follows:

Let x = grams malic acid in 100 cc.

y = grams tartaric acid in 100 cc.

a = polarization of the solution in degrees V. in a 200 mm tube after treatment with uranyl acetate.

c = grams of oxalic acid ($C_2H_2O_4 + 2H_2O$) formed by oxidation of the acids in 100 cc.

Then $-27.77 + 10.61y = a$ (1)

$1.90 + 1.68y = c$ (2)

Solving for x and y ,

$$x = -0.020a + .233c$$

$$y = .023a + .331c$$

DETAILS OF THE METHOD.

DETERMINATION OF THE ROTATION

1. Measure 85 cc of the solution under examination into a 100 cc graduated flask, render the solution slightly alkaline to litmus paper with sodium hydroxid, add five grams of sodium acetate and shake until dissolved. Reacidify the solution to litmus paper with a strong solution of citric acid, adding a slight excess of the acid, cool to room temperature and dilute to 100 cc. Treat about 30 cc of this solution with powdered uranyl acetate, transfer to a suitable container and shake for three hours with a mechanical shaker. Add enough uranyl acetate so that a small amount remains undissolved after three hours shaking. From two to three grams are usually sufficient. If the uranium salt dissolves more must be added. Filter through a folded filter and polarize if possible in a 200 mm tube. After polarizing, agitate the solution for an hour longer with uranyl acetate and again polarize to determine whether a maximum rotation has been obtained. Calculate the reading in degrees Venzke to the basis of the original solution and designate as (1).

2. Treat about 50 cc of the original solution with dry powdered normal lead acetate until no further precipitation results; avoid excess of the precipitant. A centrifuge can be used to

advantage in settling the precipitate. Filter through a folded filter and test the filtrate with a small crystal of lead acetate to determine whether precipitation is complete. Remove the excess of lead with powdered anhydrous sodium sulphate, filter until clear and polarize in a 200 mm tube. Designate this reading as (2).

3. Polarize at room temperature with white light, taking care that all solutions are polarized at the same temperature. Make at least six readings on each solution and take the average of these. Calculate all readings to the basis of a 200 mm tube. The algebraic difference between (1) and (2) in degrees Ventzke will give the combined effect of the rotations of the uranium complexes of both malic and tartaric acids. In the absence of optically active substances other than malic and tartaric acids reading (2) need not be made.

DETERMINATION OF THE AMOUNT OF POTASSIUM PERMANGANATE REDUCED

In the absence of any other substance other than malic and tartaric acids which are capable of reducing potassium permanganate, the amount of permanganate reduced is determined as follows:

Render a measured portion of the solution containing 0.2 to 0.5 g. of total malic and tartaric acids alkaline with sodium hydroxid and add an excess of about three grams of the alkali. Treat with 50 cc of 1.5% potassium permanganate and heat on the steam bath at 100° for one half hour. At the end of that time the solution should have a decided blue-black or purple color. If the solution turns green or colorless above a layer of brown precipitate at any time during the course of the oxidation more standard permanganate in measured portions must be added until the blue-black or purple color remains throughout a half hour period of heating. The oxidation is then complete. Acidify the hot solution with about 50 cc of 10% sulphuric acid and run in standard oxalic acid (5% is convenient) from a burette until the solution is colorless. Titrate back any slight excess of oxalic acid with 1.5% permanganate until a permanent pink

color is obtained. Calculate the total weight of permanganate used in the oxidation by subtracting the permanganate equivalent of the oxalic acid used from the total amount of permanganate added.

DETERMINATION OF THE OXALIC ACID FORMED

In the presence of other substances which reduce potassium permanganate but do not form oxalic acid the procedure is as follows:

Oxidize the solution with alkaline potassium permanganate in the manner described above. A standard solution of permanganate need not be used in this case but an approximately 1.5% solution is convenient. Cool the blue-black or purple alkaline solution and treat with hydrogen peroxide until the excess of potassium permanganate is destroyed and the solution is colorless except for a brown precipitate. Transfer the resulting solution with the suspended precipitate to a graduated flask of any convenient size, dilute to the mark and mix well. Filter through a folded filter without washing and pipette the largest possible aliquot of the clear filtrate into a beaker; strongly acidify with about 50 cc of 10% sulphuric acid, boil vigorously for some time to remove the excess of hydrogen peroxide and titrate hot with standard permanganate to a faint pink color. One cc of 1.5% potassium permanganate is equivalent to 0.0299 grams of oxalic acid, $C_2H_2O_4 \cdot 2H_2O$. The oxalic acid in the solution may also be determined by precipitation as calcium oxalate in the usual manner. In this case the aliquot portion of the filtrate which is used is acidified slightly with acetic acid and the oxalic acid is precipitated with calcium acetate.

In fruit juices and solutions containing sugars, add about three volumes of 95% alcohol to 50 cc of the solution and precipitate the mixed acids with normal lead acetate. Collect the precipitate (conveniently with a centrifuge), wash with 80% alcohol until free from sugars and decompose with dilute sulphuric acid. Filter off the precipitate of lead sulphate, remove the alcohol by evaporation and oxidize the acids in the solution as described above.

Calculate the total rotations and the amount of potassium permanganate reduced or of oxalic acid formed to the basis of 100 cc of the original solution and substitute the values so obtained in the proper equation, taking care to preserve the algebraic sign of the rotation.

DISCUSSION OF RESULTS

The methods suggested above for the determination of malic and tartaric acids have been applied to a number of aqueous solutions containing amounts of the acids which were unknown to the analyst and also to ciders containing added tartaric acid. The accuracy of the methods may be judged by referring to Tables IV and V in which the results are collected.

The last two determinations recorded in Table IV were made on ciders containing added tartaric acids. The other determinations shown in this table were made on aqueous solutions. In this table the total amount of potassium permanganate reduced was determined in all cases. In the two determinations recorded in Table V, which were made on apple cider, the amounts of oxalic acid formed were determined directly. Where cider was used for the determinations, the amount of malic acid contained therein was determined by titration and by the uranyl acetate method before the addition of tartaric acid.

Attention must again be called to the fact that the presence of substances which form oxalic acid on oxidation with alkaline potassium permanganate and which cannot be separated from malic and tartaric acids by precipitation with lead acetate interferes with the determination.

TABLE IV
*Determination of Malic and Tartaric *Acids*

| Malic Acid present g. per 100 cc. | Tartaric Acid present g. per 100 cc. | Rotation of acids after treatment with uranyl acetate (Original dilution) ° V. | Potassium permanganate reduced by acids in 100 cc. grams. | Malic Acid found g. per 100 cc. | Tartaric Acid found g. per 100 cc. |
|-----------------------------------|--------------------------------------|--|---|---------------------------------|------------------------------------|
| 0.46 | 1.96 | +24.3 | 5.40 | 0.48 | 1.89 |
| 0.83 | 0.60 | -11.8 | 3.54 | 0.83 | 0.57 |
| 0.47 | 0.98 | + 7.3 | 3.34 | 0.44 | 0.99 |
| 0.59 | 0.74 | - 1.6 | 3.21 | 0.58 | 0.74 |
| 0.24 | 1.24 | +17.5 | 3.22 | 0.23 | 1.22 |
| 0.52* | 0.62 | - 1.8 | 2.03 | 0.51 | 0.63 |
| 0.43* | 0.51 | - 9.2 | 2.43 | 0.55 | 0.45 |

TABLE V

| Malic Acid present g. per 100 cc. | Tartaric Acid present g. per 100 cc. | Rotation of acids after treatment with uranyl acetate (Original dilution) ° V. | Oxalic acid formed from acids in 100 cc. grams. | Malic acid found g. per 100 cc. | Tartaric Acid found g. per 100 cc. |
|-----------------------------------|--------------------------------------|--|---|---------------------------------|------------------------------------|
| 0.43 | 0.51 | - 9.2 | 1.42 | 0.51 | 0.68 |
| 0.60 | 0.59 | - 5.2 | 2.15 | 0.60 | 0.59 |

SUMMARY

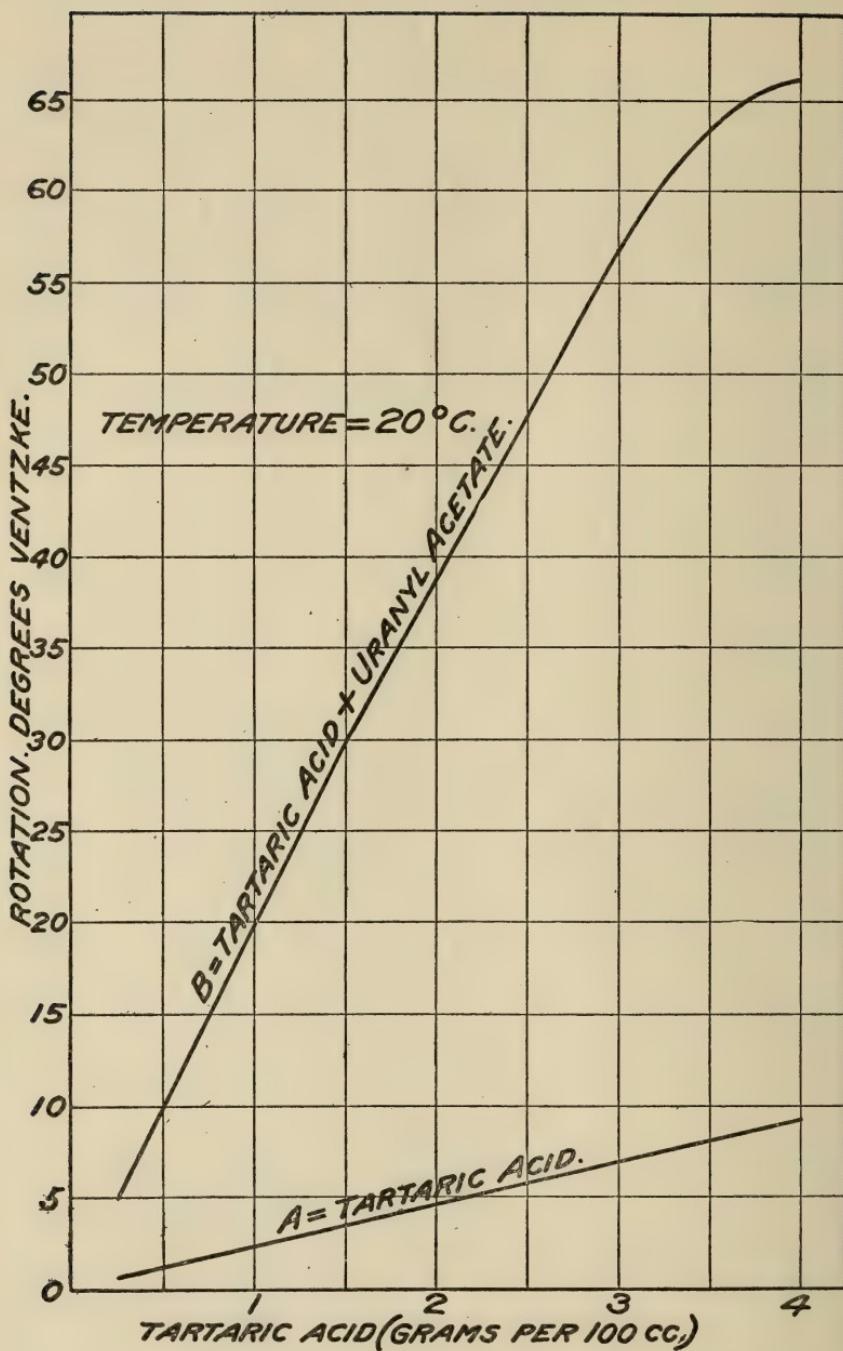
The method suggested herein for the determination of malic and tartaric acids depends on the facts:

(1) That the optical rotations of both acids are increased independently of each other when treated with uranyl acetate under definite conditions.

* Determinations on ciders containing added tartaric acid.

(2) That both acids may be oxidized quantitatively to oxalic acid by heating with potassium permanganate in alkaline solution.

Knowing the total rotation produced by these acids on treatment with uranyl acetate and either the amount of oxalic formed by oxidation or the amount of potassium permanganate reduced, it is possible to calculate the amounts of malic and tartaric acids present in a solution. The presence of substances which form oxalic acid on oxidation and which cannot be removed before treatment with potassium permanganate interferes with the method.



(*Abstract*)

THE SPECIFIC GRAVITY OF CITRUS FRUIT AS A FACTOR IN THE SEPARATION OF FROZEN FRUIT

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An extended series of experiments reporting the Specific Gravity of Sound Oranges (5 varieties) and Sound Cured Lemons (2 varieties) in terms of Percentage of Fruit floating in alcoholic solutions of various strengths. The Specific Gravity varies with the Growing District, the Variety, the Size, and the Time of Picking. The limits of variation are too great to allow of the use of any method, dependent upon the Specific Gravity of the fruit, for the accurate commercial separation of frozen from sound fruit although any lot of partly frozen fruit can be bettered by proper treatment in alcoholic solutions of the proper gravity. Tables showing results of attempted separation by floating fruit in 160 Proof alcohol and subsequently putting that fruit which floats under diminished pressure and then refloating in the same solution are given. Tables showing proximate analyses of Sound and Frozen Oranges of various specific gravities are given to show additional factors which influence the specific gravity of the fruit.

(*Abstract*)

THE GASES EVOLVED FROM ROASTED COFFEE, THEIR COMPOSITION AND ORIGIN

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It was observed that ground roasted coffee packed in a container exhausted to 183 mm. pressure gave off gas in sufficient amount to overcome the vacuum and produce 253 mm. additional pressure on the cans. Coffee packed under normal pressure gives off the same kind of gas but to a less amount and in different proportions although the final pressure developed is practically that of coffee packed under diminished pressure. Coffee packed under diminished pressure gives off more carbon dioxide and less carbon monoxide than that packed under normal pressure, the gases as they stand in the container showing 81.1% CO₂ and 4.6% CO in the container sealed under diminished pressure as against 62.8% CO₂ and 4.7% CO in containers sealed at ordinary pressure. The gas is believed to be due to the decomposition, through the roasting process, of glucoside-like bodies which occur in the green bean. The products of the decomposition are; first, sucrose and a radical which eventually becomes a fixed oil; second, the sucrose again breaks down into a glucoside-like body, probably a caramel compound, which in turn decomposes to produce the gases which are given off by the coffee. The bodies are not glucosides, but behave, in general, like glucosides.

NATIONAL CONTROL OF FOOD IN CANADA

DR. A. MCGILL, F. R. S. C.
Chief Analyst to the Inland Revenue

In my report of May 5th 1909, I gave a brief synopsis of our Food Laws and the regulation obtaining for their enforcement. No important changes, either in the laws themselves or in the regulations, have been made during the intervening three years, except as regards the Adulteration Act.

Minor changes in other Departments of Food control may be briefly referred to.

MILK TEST ACT

The Milk Test Act of 1911 provides for the correct marking of volumetric glass-ware used in Creameries.

MEATS AND CANNED FOODS ACT

The Meats and Canned Foods Act of 1907 was amended in 1910 as regards many particulars. Perhaps the most important is that which forbids the use of any dye, drug, preservative or seasoning which has not been approved in writing by the Veterinary Director General.

The scope of the Adulteration Act as revised in 1907 is such as to include Drugs, Fertilizers, Insecticides, and certain Paint materials in addition to Foods for man and cattle.

PROPRIETARY AND PATENT MEDICINE ACT

In 1908, the Proprietary and Patent Medicines Act was passed. This Act may be regarded as, in some sense, complementary to the Adulteration Act, in so far as this refers to Drugs.

The chief provisions of this Act are as follows:

1st. Proprietary or Patent Medicines are defined as all artificial remedies or prescriptions manufactured for the internal use of

man, the name, composition or definition of which is not to be found in the British Pharmacopœia, the Codex Medicamentarius of France, the Pharmacopœia of the United States, or any foreign pharmacopœia approved by the Minister, or any formulary adopted by any properly constituted pharmaceutical association representing the Dominion of Canada, approved by the Minister; or upon which is not printed in a conspicuous manner, and forming an inseparable part of the label and wrapper, the true formula or list of medicinal ingredients.

2nd. It forbids the manufacture, importation or sale of any proprietary or patent medicine containing Cocaine; also any containing Alcohol in excess of the amount required as a solvent of the Drugs present.

3rd. It forbids the sale of such Medicines as contain the following Drugs.

SCHEDULED DRUGS

Acetanilide and other coal tar products.

Aconite and its preparations.

Arsenical preparations.

Atropine.

Belladonna and its preparations.

Cantharides.

Carbolic acid.

Chloral hydrate.

Chloroform.

Conia and compounds thereof.

Corrosive sublimate.

Cotton root.

Croton oil.

Digitalis and derivatives.

Ergot.

Essential oil of mustard.

Ether.

Hellebore.

Heroin.

Hyoscyamin and its preparations.

Hyoscyamus and its preparations.

Indian hemp.
Morphine and its preparations.
Nux vomica and its derivatives.
Opium, its preparations and derivatives.
Pennyroyal.
Phenacetine.
Prussic acid.
Savin and preparations thereof.
Strychnine and its preparations.
Sulphonal.
Tansy.
Tartrate of antimony.
Veratria.

FOODS FOR CATTLE

Foods for cattle were made the subject of special legislation in 1909. The Feed Stuffs Act requires all Cattles feeds to be registered, and their minimum value in proteids and fats, and maximum fibre content, to be guaranteed by the manufacturer.

Only such feeds are exempt from registration whose value is apparent to the buyer; *e. g.*, Hay, Straw, Roots, etc.; and such as are sold under a name which is defined for legal purposes under Section 26 of the Adulteration Act, Bran, Shorts and Chop-feeds come under this Category.

FERTILIZERS

Fertilizers were also specially controlled by the Fertilizer Act of 1909. These must be registered and guaranteed as to value in Nitrogen, Phosphoric Acid and Potash. Exception is made of Barnyard manure.

FOOD STANDARDS

Progress has been made in the legalizing of Food Standards under the Adulteration Act. The following are now in force.

| | |
|------------------------|-----------------|
| Meat & Meat Products | since Nov. 1910 |
| Grain & Grain Products | since Dec. 1910 |
| Milk & Milk Products | since Dec. 1910 |

| | |
|--------------------------------------|------------------|
| Beverages, Alcoholic & Non-alcoholic | since March 1911 |
| Maple Sugar & Syrup | since April 1911 |
| Edible Vegetable Oils | since May 1912 |

For purposes of inspection, Canada is divided into sixteen districts, each having a resident inspector, whose duty it is to make periodical collection of samples of Foods and Drugs sold within his territory, on instructions from Ottawa. It is probable that in the near future a re-distribution of districts will be made, to facilitate and cheapen inspections.

Publication of the results of Analysis is made by issue of Bulletins from time to time. At the date of my last report, 179 bulletins had been published, since that date 62 additional bulletins have been issued, making the total number 241. (August 1912.)

These are distributed to Members of Parliament, Editors of Newspapers, Libraries, and to many correspondents, whose names are upon our mailing lists.

They are available to any one on request.

Of the 62 bulletins issued, 43 deal with foods; 12 with drugs; 4 with Commercial Fertilizers and 3 with Cattle Feeds. A decided improvement in the character of both Foods and Drugs is traceable to the operation of the Adulteration Act, since 1876, when first it became operative. This is capable of Statistical proof; but the full effectiveness of such legislation, as a protection against fraud, is not demonstrable, and can only be inferred by considerations which force themselves upon the mind of every observant and thoughtful individual.

COLTURA ED INDUSTRIA DELL'AMARASCO IN DALMAZIA

E. NICOLIC

Zara

Fra i più importanti prodotti industriali della Dalmazia è certo il *Maraschino*, il quale viene esportato per tutti i paesi e, purtroppo, oggidì in tutti i paesi consumatori si cerca di imitarlo in vario modo, sia impiegando eteri artificiali, sia il distillato di altre frutta che contengono principi aromatici affini. Il Maraschino genuino che acquistò tanta fama, è un rosolio preparato a base del distillato etero di certe specie di *Prunus*, rispettivamente di *Cerasus*, che crescono parte selvatiche, parte coltivate in Dalmazia e vi son dette "Amarasche."

Non solamente dal grosso pubblico e da molti botanici, ma da quelli stessi che con più o meno di competenza, scrissero finora del: Rosolio Maraschino di Zara, si crede tuttavia che la *Amarasca*, dalla quale si prepara il celebre liquore, sia il frutto del *Prunus Mahaleb L.* Ma questo arbusto arborescente, che abbonda spontaneo dal Mediterraneo alle Alpi Centrali, e da queste fino alla penisola Celtiberica, non è invece la pianta che in Dalmazia produce *l'Amarasca*. Questa è un prodotto culturale, dovuto all'onesto di una particolare varietà del *P. Cerasus* sul *P. Mahaleb* stesso.

Dalla varietà del *P. Cerasus* prescelto, dipende pure la qualità dell'Amarasca che si ottiene, perchè queste varietà del *P. Cerasus*, sono a lor volta, prodotti d'incrociamento più o meno remoto della forma tipica fondamentale, con altre affini. Esse ritengono quindi in vario modo e differente misura, le qualità delle piante da cui derivano; modificate dall'influenza degli agenti topici e meteorici.

Vi ha perciò in Dalmazia di varie sorta d'amarasche; alcuna per la sottile delicatezza del profumo, ricercatissime e tipiche, altre poi, derivate per lo più da vivai recenti e poco razionali, decrescenti per regressione verso le forme iniziali del *P. Cerasus*,

e punto convenienti alla fabbricazione del Rosolio o alla preparazione di conserve. Le prime qualità, le migliori dunque, son quelle che derivano dall'inesto di una costante varietà del *P. Cerasus L.* classificata spesso in vari modi, cioè: *P. acida Ehrh.*, *Cerasus Marasca Host.*, *C. Caproniana*, *D. C.* e *P. Marasca* del nostro Visiani.

Lo stesso *P. Mahaleb* che serve da base dell'inesto si trova in vario numero di varietà topiche. Una di queste, con foglie cordato-acuminate, big landulate alla base, corteccia glabra, chiazzata a chiaro-scuro e di legno profumato è la più ricercata. Essa abbonda nei siti alpestri e soleggiati della Poglizza e Vodizze, località vantaggiosamente note, per l'eccellenza del loro prodotto.

La coltura dell'amarasca in Dalmazia è certamente antica, e tanto che una tradizione popolare della Poglizza la vorrebbe far risalire ai tempi di Diocleziano, che l'avrebbe introdotta nelle valli ubertose di Srigniñe e sugli aprichi pendii di Jesenizze. Ma negli antichi autori Romani non troviamo le prove storiche di questa leggenda nè argomenti che ci possono persuadere, che i Romani conoscessero la nostra Amarasca, e la coltivassero a scopo industriale o casalino. Plinio solamente accennando alle ciriege "Peregrinae" importate in Italia da Lucullo, dice che ve n'erano pure nell'Illirio d'indigene o selvatiche, come le: "Macedoni" ed i "Camecerasi," che in quel paese venivano disseccati in vasi e conservati come l'oliva.

Così pure incerta è l'origine del nome: "Amarasca." In Plinio ed in altre fonti romane si riscontra qualche cosa di simile nei nomi di "Amaraco" e "Marisco" che indicano piante e frutta più o meno note ad aromatiche, ma che assolutamente non si possono attribuire alla nostra "Amarasca."

Nell'antico Illirio e tuttavia nell'odierna Albania, col nome di "Maraj" ed "Amaraj" si denotavano, e si denotano alcune piante odorose e profumate, ma non l'Amarasca. Vi fu pure chi credette di poter chiamare l'amarasca "Almarasco" e quindi farla credere introdotta dagli Arabi.¹ È da notarsi però che anche da noi in Dalmazia questo nome ed i suoi derivati non

¹ Nelle vecchie farmacopee, che attinsero alle fonti arabiche l'Amarasco spontaneo è detto: "Almahaleb" da cui derivò il "Mahaleb dei botanici, per indicare la specie selvatica, indigena dell'Europa meridionale: in Dalmazia detta: "Raselka"

sono esclusivamente e specificatamente riservati all'Amarasco ed ai suoi prodotti, perchè abbiamo delle prelibate ed elettissime sorta di vini, assai celebrati per la delicatezza del loro profumo, che son detti: "Maraschini" nè hanno punto sapore o qualsivoglia altra qualità del Rosolio Maraschino. E questo semplice argomento potrebbe pur valere più d'ogni altro a farci ammettere che il nome d'Amarasca derivi dall'antica radice illirica significante: Pianta o frutto aromatico e profumato.

Il modo, e quando l'Amarasca principiò a dar vita a questa industria del Maraschino, non pare che lo si possa determinarlo con stabili date, ma dei fattori primitivi, che contribuirono poco a poco a svilupparla, si può raccogliere qualche interessante notizia dalle vicende storiche del paese.

I Romani, che gustavano il "Garo," come liquore squisitissimo, che ignoravano la distillazione e l'uso domestico dello zucchero, non furono certamente i nostri maestri nell'arte di confezionare i rosoli, e molto meno in quella di trar profitto dall'amarasca.

Questa incominciò ad avere una certa considerazione assai più tardi, quando i Greci di Costantinopoli, attinsero dalla farmacopea arabica l'uso dello zucchero e dell'Alambicco, nonchè la preparazione dei Roob, dei Giulebbi, degli sciroppi, delle conserve, dei liquori e delle essenze, che con l'amministrazione e le costumanze loro introdussero nelle città dalmatiche dove governarono dal VI al XI secolo.

Nelle antiche farmacopee degli Arabi vi troviamo cose che l'Europa romana non conosceva, ma che nel medioevo i medici greci i farmacisti, i monaci loro, presto diffusero nei paesi del Mediterraneo; e gli Alchimisti poi nella restante Europa. Il loro Vinum Sublimatum, l'acqua vitae, l'Elisir Vitae, la quinta essenza, passarono ben presto dall'officina farmaceutica all'economia domestica, e da questa all'industria ed alla tecnologia.

Perciò il germe primitivo di questa nostra industria del Maraschino, non venne, come generalmente si crede, e fu scritto da alcuni nostri autori, dall'Italia ma dall'Oriente, ed in un'epoca in cui nei paesi dell'altra sponda Adriatica, l'uso dell'Alambicco, non era ancora uscito dalle oscure officine apotecarie. Preziosa conferma di quest'affermazione è il bassorilievo dello stipite istoriato nel portale della chiesa di Trau, raffigurante l'uso dell'

Alambicco. La chiesa è costruzione del XII secolo, ma il portale, a quanto dicono persone competenti, è opera assai più antica, e quindi di grande valore per dimostrare come l'arte distillatoria fosse in quei tempi remoti, diffusa in Dalmazia.

Vi ha pure, ma meno antico, un altro esempi o di ciò nel capitello del palazzo rettorale a Ragusa, noto come: Capitello dell' Alchimista.

Ma le prime notizie sulla produzione di un liquore dolce squisito, e già *celebre nel mondo*, per la delicatezza del suo profumo, le troviamo nella laude latina in onore di Sebenico, del poeta Giovanni Nardino del XVI secolo, e quindi nel suo parafrasatore Pietro Difnico, che quella laude volgarizzo' in islavo, alcuni anni più tardi.

Nel secolo XVIII, il Maraschino di Zara, e particolarmente quello della fabbrica Drioli, ha già buona fama ben oltre i confini della provincia e dello stato. Nel 1772 l'illustre naturalista italiano A. Fortis scrive d'aver veduto a Vodizze, a Trebocconi i vasti impianti, che forniva l'Amarasca alle fabbriche di Zara. Nella seconda metà del XVIII secolo, la Serenissima favorisce l'industria zaratina del Maraschino con l'esenzione di dazi e di tasse. Specialmente la volle libera dal dazio del trentesimo, istituito nell'anno 1755, e ciò fece con speciale terminazione, onde salvaguardare questa fiorente industria dalle angherie degli appaltatori di dazi. Fu del pari favorita dalla istituzione della *fiera franca* (1691) alla quale affluivano a Zara i mercanti dell'Istria del Quarnaro, della Croazia, della Bosnia, ma molto più numerosi quelli di Ravenna, Rimini, Pesato, Ancona, Fermo, Sinigaglia e del Napoletano. In sul cadere della repubblica di Venezia, v'erano ben undici fabbriche di Maraschino a Zara, che per la via di Venezia, di Trieste, di Fiume e di Ancona esportavano lucrosamente il loro prodotto.

Le guerre napoleoniche, il blocco continentale, furono fatali alla prosperità di quest'industria, e quindi nel periodo napoleonico scema rapidamente il numero delle fabbriche.

Col ritorno del governo austriaco ritornano le condizioni favorevoli, perchè non solo si riaprono i confini delle provincie austriache allo smercio, ma quelli pure dello Stato pontificio del Napoletano, dipendenti in linea doganale dall'Austria.

Le vicende politiche del 1859 e del 1866, non esercitarono su quest'industria una immediata e visibile influenza, anzi dopo quest'epoca sorse nuove fabbriche minori, ed altre come la "Luxardo," e la "Vlahov" oltre alla secolare "Drioli" salirono a grande rinomanza e vera celebrità mondiale.

E così pure in altre città della Dalmazia, specialmente a Spalato sorse nuove fabbriche, che in breve si affermarono vantaggiosamente, per ragguerdevole produzione e bontà del genere.

Oggigiorno questa nostra industria pare floridissima pero combatte un aspra lotta per mantenersi all'altezza che ha raggiunto mercè l'attività e l'energia delle ditte produttrici, perchè le primitive condizioni materiali si sono mutate a svantaggio dell'industria stessa.

Fino quasi al 1859 si importava cioè ancora lo zucchero coloniale greggio, detto "Mascaba" che si depurava nelle fabbriche stesse e l'alcol impiegato si otteneva rettificando le acquavite indigene.

In seguito alle restrizioni fiscali nell'importazione di zucchero coloniale, ed alle difficoltà di ottenere l'alcol di vinacce puro esente di alcol superiori; nelle quantità che oggi esige questa industria, la preparazione subì qualche modifica nel dettaglio, pure mantenendo nell'essenza la sua forma originale.

(*Abstract*)

STUDIES ON CHICKEN FAT

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INFLUENCE OF TEMPERATURE ON THE LIPOLYSIS OF ESTERS

The aqueous extracts of the crude abdominal fat of chickens were incubated with esters at the temperature of the incubator, 40°C., of the refrigerator (average temperature 17.2°C.), of a mechanically refrigerated chillroom at 0.°C., and of a mechanically refrigerated freezer at -9.4° to -6.7°C. The period of incubation varied between the extremes of three days in the incubator and one hundred fifty-one days in the freezer. The greatest splitting of the esters by the lipase took place in the incubator, the least in the freezer, and between these two extremes lay the splitting in the refrigerator and in the chillroom.

When the increase in acidity, due to the action of lipase for three days in the incubator at 40°C. is taken as a standard for comparison, and when the increase in acidity, due to the action of the enzyme for three days in the refrigerator, for eighteen days in the chillroom and for forty-five days in the freezer are compared with this standard, the following data were obtained in the lipolysis of ethyl butyrate. This ester was hydrolyzed in the incubator two and one-half times as fast as in the refrigerator, twelve times as fast as in the chillroom and forty times as fast as in the freezer. Similar results were obtained in the lipolysis of ethyl acetate, ethyl benzoate, and amyl salicylate. Although the rate of lipolysis is decreased by lowering of the temperature, yet lipolysis takes place even at the temperature of the freezer, when the reaction-mixture is frozen solid.

(Abstract)

STUDIES ON CHICKEN FAT

THE HYDROLYSIS OF CHICKEN FAT BY MEANS OF LIPASE

The crude abdominal fat was extracted by means of ethyl ether, and the fat was recovered by distilling off the solvent. The tissues which remained in the thimble of the extractor were extracted with glycerol to obtain a solution of the lipase. Portions of the glycerol extract of the enzyme were mixed with portions of the extracted fat and were incubated at 40°C. for seventy-two hours. Blank experiments were also made upon the heated glycerol extract. Toluol was used as a bactericide. After incubation the acid value of the determination proper and of the blank was determined. In every case the determination proper had a higher acid value than the blank, therefore, the lipase had produced hydrolysis of the chicken fat in spite of the fact that a glycerol extract of the enzyme was used. When conditions were made more favorable for the action of the lipase by adding water to the substratum during incubation, the rate of hydrolysis was increased.

(Abstract)

STUDIES ON CHICKEN FAT

JOSEPH S. HEPBURN

THE OCCURRENCE OF CATALASE, OXIDASES AND REDUCTASES
IN THE FAT OF THE COMMON FOWL (*GALLUS DOMESTICUS*)*Catalase*

Thirty samples of chickens were examined, including birds just killed and retaining animal heat, one kept in the refrigerator, one "green struck" bird in the incipient stages of putrefaction, and one in an advanced state of putrefaction, as well as fowls at various stages of their marketing. In every case both catalase and lipase were present. However, the activity of the catalase is apparently more or less independent of the period of keeping of the birds after death.

Oxidizing Enzymes

The chickens examined included birds kept for various periods of time at temperatures varying from that of the room to that of the mechanically refrigerated freezer, as well as fowls at various stages of their marketing. For the detection of oxidases, pyrogallol, hydroquinone, pyrocatechin, p-phenylene diamine and p-phenylene diamine plus α -naphthol, were used. For the detection of oxidases plus peroxidases the oxidase reagents were used with the addition of hydrogen peroxide. The aqueous extract of the crude abdominal fat was incubated with these reagents for eighteen hours at 40°C. Blank experiments were also made on the boiled extract and toluol was used as a bactericide.

The reaction was considered positive in each case when (1) a color developed in the determination proper while the blank remained colorless, (2) the color of the determination proper was

distinctly more pronounced than the color of the blank. In the experiments, to which hydrogen peroxide had not been added, oxidase alone caused the development of a color: in the experiments to which hydrogen peroxide had been added, both oxidase and peroxidase could give rise to the color; However, the two sets of experiments were carried out side by side, and it thus became possible to compare the intensity of the color produced by the extract with any given reagent with and without the addition of hydrogen peroxide; a more intense color in the flask containing peroxide would demonstrate the presence of peroxidase which had produced the excess of color over and above that produced by the oxidase in the absence of hydrogen peroxide.

Oxidases were present in the fourteen samples examined; in thirteen of these experiments, one or more of the reagents gave a more intense color when hydrogen peroxide was added to the reaction mixture than when it was omitted; therefore, peroxidases were also present.

Reductases

The research included within its cope tests for both simple and aldehyde reductases in the crude abdominal fat. For the detection of simple reductases, the aqueous extract of fat was mixed with methylene-blue solution, using sodium fluoride as a bactericide. For the detection of aldehyde reductases Schardinger's methylene blue-formalin solution was used. Blank experiments were made in all cases on the boiled extract. Both determinations proper and blanks were incubated at 40°C. for eighteen hours under anaërobic conditions. In two of the seventeen experiments simple reductases were found and likewise in two of seventeen samples aldehyde reductases occurred. Therefore, both species of reductases may occur in crude fat.

(*Abstract*)

ON A STUDY OF THE ENZYMES OF THE EGG OF
THE COMMON FOWL

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The work was done on fresh eggs, fertilized and unfertilized, stale eggs of unknown history and eggs of known history, kept for varying lengths of time under definite conditions.

Experiments were made to determine the presence of lipase, catalase, reductase, pepsin and trypsin. No evidence of reductase, pepsin or trypsin could be obtained. Lipase and catalase were found.

In general it was observed that the lipase content of fresh eggs is low. There is a fairly regular increase as the egg deteriorates. As the egg incubates at high temperatures the increase in lipase content is more noticeable in the case of fertile than in the case of unfertile eggs although it is apparent in both cases. Fresh eggs kept at 0°C. for three months showed an increase in lipase at the end of the second month but no further increase at the end of the third month.

The study of the catalase content of fertile and unfertile eggs showed that the increase of this enzyme in fertile eggs as incubation proceeds is very great. While there is a slight increase in the unfertile maintained at incubator temperatures, it is comparatively slight. For instance, in some cases unfertile eggs kept for several weeks at incubator temperatures showed little more catalase than the average fresh eggs while unfertile eggs at the end of a week showed a catalase content ten times as great.

The amount of loosely bound nitrogen as estimated by the Folin method was also determined. Apparently, in the case of unfertile eggs a very noticeable and quite regular increase in the amount of loosely bound nitrogen takes place with time. While

in the case of fertile eggs held at incubator temperatures the increase is very slight for at least 200 hours. Considering the content of loosely bound nitrogen as a criterion of protein decomposition this is not surprising since, in the first case, the heat would be expected to increase catabolic processes, making for simpler nitrogen compounds while, in the second case, it introduces metabolic or upbuilding processes.

(*Abstract*)

THE DETERMINATION OF ARSENIC

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Various modifications have been used and are suggested in the Gutzeit method as modified by Sanger and Black. Conditions essential to the correct estimation of small amounts of arsenic are given. The importance of the reduction of arsenates to arsenites in all arsenic estimations, previous to the reduction by nascent hydrogen, is emphasized. The use of 0.75 gm. potassium iodide in 50 cc. of an acid solution of 10% hydrochloric or 1.4 sulphuric, 4 or 5 drops of a 40% stannous chloride solution and heating for ten minutes near the boiling temperature, is recommended as superior and more generally applicable than the sulphur dioxide reduction. The stannous chloride further serves as sensitizer and prevents the retentive effects of iron salts or arsenic. The mercuric bromide strips are found to be preferable for arsenic stains because of their permanence and are preserved without development. Larger amounts of arsenic from 0.1 mg. to 10 mg. or more are determined by a new method which consists in passing the arsine through mercuric chloride solution. This solution is boiled with the precipitate for thirty minutes until it is entirely converted to calomel. The calomel may be weighed or estimated by adding potassium iodide, excess of iodine, and titrating the excess with thiosulphate. Arsenic in amounts from 1 mmg. to 10 mg. or more is precipitated quantitatively by a new method which consists in adding a certain excess of sodium phosphate and precipitating the whole with magnesia mixture. This method serves for the separation of arsenic from large amounts of inorganic and organic substances including antimony. By adding the proper amounts of am-

nium chloride and tartaric acid and a second precipitation, arsenic in amounts as small as one part per million parts of antimony can be estimated.

An outline of methods for determining arsenic in shellac, hops, gelatine, copper, etc., is given.

THE CHLORAL HYDRATE TEST FOR CHARLOCK

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Wagge¹ appears to have originated this test—at least he applied it to the detection of charlock in mustard flour nearly twenty years ago. It consists in mounting a portion of the material on a microscopic slide in chloral hydrate solution (8:5) and noting the carmine red color formed in and about fragments of the hulls of charlock. The reaction takes place slowly in the cold but almost immediately on gentle heating. None of the true mustards give this color.

Under the compound microscope it may be seen that the color is due to the partial solution of the dark colored contents of the palisade cells which form the third layer of the hull. Even without this color reaction, identification of charlock is not difficult for the microscopist as none of the true mustards have this dark substance in the palisade cells, furthermore, as shown by Collins,² the epidermal cells, especially when viewed with polarized light, are characteristic. The compound microscope, however, is not essential, or even desirable, for the color test since, as proposed by K. G. Winton, a better idea of the proportion of charlock is gained by examination with a strong lens, holding the mount in front of a piece of white paper before a strong light.

For years the writer has applied this test successfully until recently when a new lot of chloral hydrate solution was found to give only a faint reaction—so faint, indeed, as not to be decisive. Thinking that the reagent was impure, other lots were tried, with the same result, while a solution made up some months previous invariably gave sharp reactions, indicating

¹ Ber. d. Pharm. Ges., 1893, 153.

² A Note on Mustards and their Chief Adulterant Charlock. Swarthmore, Pa., 1910.

that the reagent is only active after long standing. In searching for the reason for this difference, it was soon found that the reaction of the fresh solutions was in all cases neutral, whereas that of the old solution was strongly acid. This is in accordance with a statement made in the United States Pharmacopoeia.

As the acid formed is doubtless hydrochloric acid, it was reasoned that the addition of this acid to fresh chloral hydrate solution should bring about the same result as aging, and further experiment proved this to be the case. A mixture of one volume of concentrated hydrochloric acid with twenty volumes of chloral hydrate solution of the usual strength gave more striking reactions than any obtained with the aged solution.

Further experiments were made to determine whether hydrochloric acid alone or other reagents would produce the same results. It was found that the acid alone gave a faint but unsatisfactory reaction. This failure was attributed to the lack of penetrating power of the acid as compared with chloral hydrate solution which is a well-known clearing agent, penetrating cell walls and dissolving cell contents. A mixture of twenty volumes of glycerin (another well-known clearing agent) with one volume of concentrated hydrochloric acid was found, however, to give a satisfactory color reaction after cautious heating. Syrupy zinc chlorid solution mixed with hydrochloric acid in the same proportion also gave the carmine red color on heating, from which it appears that organic matter is not essential for the test.

To learn whether hydrochloric acid is essential, tests were made using sulphuric acid, syrupy phosphoric acid and a syrupy solution of citric acid. Of these, the sulphuric acid was found unsatisfactory because charring set in before reactions could be noted, but phosphoric acid and citric acid gave excellent reactions. It seemed unnecessary to search further as it was evident that the color could be produced by various acid solutions, provided they possessed penetrating power. In all cases heating was essential for a sharp and immediate reaction, acid chloral hydrate solution, however, requiring less heating than any of the other reagents noted.

For general use in detecting charlock the writer prefers the reagent prepared as follows: Dissolve 16 grams of crystallized

chloral hydrate in 10 cc of water. To the solution add 1 cc of concentrated hydrochloric acid.

In making the test, mount about 10 mg. of the mustard flour (or an equivalent amount of prepared mustard) on a slide in the reagent, heat cautiously (never to boiling) for a moment and examine under a lens. Note the proportion of fragments of hulls that acquire a carmine red color (charlock) to those not changed in color.

SUR LA PRÉSENCE NORMALE DU BORE CHEZ LES ANIMAUX

GABRIEL BERTRAND ET H. AGULHON

La présence de petites quantités d'acide borique dans les cendres du vin et de quelques végétaux a d'abord été signalée comme un fait exceptionnel, mais des recherches précises et étendues, entreprises en partie par l'un de nous,¹ ayant permis de doser entre un millième et un centième environ d'acide borique dans les cendres de tous les végétaux examinés, on doit compter aujourd'hui le bore parmi les éléments constitutifs des espèces végétales.

En est-il de même en ce qui concerne les espèces animales? Jay et Dupasquier ont cherché le bore dans un os et dans la chair musculaire du Boeuf sans en trouver.² Jay l'a cherché à nouveau dans le lait de la Vache, le sang du Boeuf et du Mouton sans plus de succès.³ Mais ces observateurs ont vu que l'urine de l'Homme, des Ruminants et du Cheval renferment plusieurs milligrammes du métalloïde par litre, de sorte que l'un d'eux a cru pouvoir écrire que le bore "introduit à très petites doses dans l'estomac des animaux, comme cela se produit quotidiennement, n'est en aucune façon assimilé et est rejeté avec les déjections."⁴

Il n'est pas impossible qu'une différence de composition élémentaire aussi profonde sépare les espèces végétales et les espèces animales mais, avant de l'admettre d'une manière définitive, il est indispensable de recourir à de nouvelles expériences, entreprises dans des conditions de grande précision et d'extrême sensibilité. L'un de nous, en effet, a montré tout récemment, en collaboration avec Medigreceanu, que le manga-

¹ H. Agulhon, Thèse deot. ès-sciences nat., Paris, 1910. On trouvera dans cette thèse la bibliographie de la question.

² C. R., t. 121, p. 260 (1895) et Bull. Soc. chim., 3^e série, t. 13, p. 877 (1895).

³ Bull. Soc. chim., 3^e série, t. 15, p. 33 (1896).

⁴ Jay, dernière citation.

nèse existe d'une manière aussi constante dans l'organisme des animaux que dans celui des végétaux, mais en proportions beaucoup plus petites.⁵ Il peut en être de même pour le bore.

Nous avons utilisé, pour trancher cette question, la méthode que nous avons publiée il y a deux ans, grâce à laquelle il est possible de reconnaître *très nettement* un demi-millième de milligramme de bore et qui peut même donner dans certaines conditions, une réaction positive avec 1/50.000 de milligramme du métalloïde.⁶

Les expériences dont nous apportons aujourd'hui les premiers résultats ont porté sur le Cobaye, le Lapin, le Mouton, le Boeuf et le Cheval.

Les organes ou tissus, recueillis et desséchés avec toutes les précautions désirables, ont été brûlés, soit par portions dans une bombe en platine à l'aide d'oxygène électrolytique,⁷ soit au four à moufle, à la température la plus basse possible. Le résidu de la combustion a été transvasé dans un petit ballon, éthérifié par l'alcool méthylique; l'éther a été distillé et saponifié par la soude, enfin la solution sodique essayée avec la curcuma et, quand il y avait lieu, c'est-à-dire quand il y avait assez de métalloïde, transformée en fluorure de bore et examinée au spectroscope.

Dans le tableau suivant, nous exprimons l'intensité relative de la réaction au curcuma par la longueur, en millimètres, de la partie de la bande colorée en rouge après 18 et 48 heures, la

⁵ C. R., t. 154, p. 941 et 1450 (1912), t. 155, p. 82 (1912) et Bull. Soc. chim., 4^e série, t. 11 (1912).

⁶ Bull. Soc. chim., 4^e série, t. 7, p. 90 et 125 (1910). Depuis cette publication, nous avons rencontré une fois de l'acide sulfurique si difficile à purifier complètement que nous l'avons remplacé par de l'acide phosphorique obtenu en mélangeant une partie d'anhydride avec une partie d'eau. L'emploi de ce nouvel acide (5 cc.) pour favoriser la formation de l'éther méthylborique présente en outre l'avantage de ne pas déplacer d'une manière appréciable l'acide chloryhdrique, ce qui serait très gênant au point de vue de la sensibilité dans le cas des cendres animales, ni l'acide azotique, encore plus gênant, qui se produit lorsqu'on opère la destruction des matières organiques par la bombe.

⁷ Voir pour l'emploi de la bombe dans les cas de ce genre: Gabriel Bertrand, Bull. Soc. chim., 3^e série, t. 29, p. 209 (1903).

solution sodique ayant été ramenée dans tous les cas, au volume final d'un centimètre cube.

| Substances analysées | Poids | | Mode de destruction | Long. color. | | Réaction spectrale |
|-------------------------|--------|-------|---------------------|--------------|-----------|-------------------------------|
| | secs | frais | | ap. 18 h. | ap. 48 h. | |
| Cobaye nouveau-né . . . | 40g. 5 | 120g. | moufle | 3 mill. | 5 mill. | |
| Lapin Peau..... | 10 | | id. | 0 | 0 | |
| id. | 10 | | id. | 0 | 0 | |
| Poils..... | 10 | | id. | 5 mill. | 8 mill. | |
| Muscles..... | 10 | 35,8 | id. | 2,5 m. | 4 mill. | |
| id. | 20 | 71,6 | id. | 3 mill. | | Nette (sur 20 gr. secs) |
| Foie..... | 10 | 39,8 | id. | 1 mill. | | |
| id. | 10 | 39,8 | bombe | 2 mill. | 4 mill. | |
| Tube digestif..... | 10 | 59 | moufle | 0 | 0 | |
| Os..... | 10 | 13 | id. | 2 mill. | 3 mill. | |
| Sang..... | 7,5 | 12 | id. | 0 | 0 | |
| Poumon..... | 6 | 12 | id. | 0 | 0 | |
| Mouton Cerveau..... | 10 | 55,5 | id. | 0 | 0 | |
| Langue..... | 10 | 34,5 | id. | 0 | 1 mill. | |
| Boeuf Cornes..... | 5 | | bombe | 3 mill. | | Très nette (sur 20 gr.) |
| id. | 10 | | id. | 5 mill. | | |
| Langue..... | 10 | 44,2 | moufle | 0 | 1 mill. | |
| id. | 24 | 106 | id. | 0 | 1 mill. | |
| Foie..... | 10 | 31,8 | id. | 0 | 0 | |
| Bile..... | 10 | 107 | id. | 2 mill. | | |
| Poumon..... | 10 | 53 | id. | 0 | 0 | |
| Coeur..... | 10 | 42 | id. | 0 | 1 mill. | |
| Cheval Langue..... | 10 | 39,5 | id. | 0 | 1 mill. | |
| Poils..... | 10 | | id. | 3 mill. | 5 mill. | Très nette (sur 30 gr.) |
| Sang..... | 10 | 46 | id. | 0 | 0 | |
| id. | 10 | 46 | bombe | 0 | 0 | |
| id. | 40 | 184 | moufle | 0 | 1 mill. | |

On voit, par ces résultats, que le bore se trouve dans l'organisme des cinq animaux que nous avons examinés. Il est relativement facile à mettre en évidence, non seulement dans les poils, les cornes et les os, mais aussi dans le foie et dans les muscles. Néanmoins, comme il fallait s'y attendre, sa proportion est toujours extraordinairement petite. Ainsi, dans les muscles du Lapin, elle doit être, d'après les essais comparatifs que nous avons tentés,⁸ d'environ 1/200 de milligramme pour 10 grammes de substances sèches, soit, par conséquent, d'environ 1 milligramme pour kilogrammes de muscles frais. Le sang, chez le Cheval, serait approximativement 10 fois plus pauvre encore que les muscles du Lapin.

⁸ En tenant compte de l'influence du chlorure de sodium.

SUR UNE NOUVELLE FONCTION DU CATALYSEUR DIT "PEROXYDASE" ET SUR LA TRANS- FORMATION BIOCHIMIQUE DE L'OR- CINE EN ORCÉINE

JULES WOLEF

Dans un travail encore inédit j'ai déjà fait ressortir le rôle nouveau que peut jouer la peroxydase lorsqu'on l'associe à divers sels et aux alcalis dans leur action sur certains phénols. Ainsi, en solution sodique faible et au large contact de l'air l'orcine peut fixer de 4 à 5 fois plus d'oxygène en présence qu'en l'absence de peroxydase. Je me propose d'établir dans le présent travail que la peroxydase est encore douée d'autres propriétés et qu'elle peut agir autrement qu'en fixant l'oxygène atmosphérique.

C'est ainsi qu'en étudiant sur l'orcine en solution aqueuse l'influence combinée de l'ammoniaque et de la peroxydase, j'ai été amené à faire quelques observations curieuses sur les conditions qui peuvent favoriser en liqueur étendue la transformation de l'orcine en orcéine, cette belle matière colorante,¹ qui est un des principes essentiels de l'orseille du commerce.

Les faits que j'ai observés au cours de mes recherches sont intéressants à plusieurs points de vue, car ils démontrent que:

1°. Si l'on soumet sous une faible épaisseur et au large contact de l'air une solution d'orcine à 2.% à l'influence de doses variables d'ammoniaque on n'obtient pas d'orcéine, même après un mois de contact, mais il se forme une substance qui colore la liqueur en rouge brun.

2°. En abandonnant, toutes choses égales d'ailleurs, la même solution dans un tube à faible diamètre, de manière à opérer sous une grande épaisseur et en limitant la surface de contact avec l'air, on observe une formation très lente, mais régulière d'orcéine.

¹ L'orcine a déjà fait l'objet d'intéressants travaux de la part de Robiquet, Dumas, Laurent et Gerhardt, de Luynes.

3°. Si toutes choses égales d'ailleurs on répète l'expérience 1° en ajoutant à la solution ammoniacale d'orcine une dose convenable de peroxydase on n'observe pas plus qu'en 1° la formation d'orcéine.

4°. Si toutes choses égales d'ailleurs on répète l'expérience 2° en ajoutant à la solution ammoniacale d'orcine une dose convenable de peroxydase la transformation en orcéine s'opère très vite et elle est déjà très avancée au bout de 4 à 5 jours.¹

Pour 1 et 2 { 2cc de solution d'orcine à 2,8%
50 mgr de AzH₂ } amener à 3c,5 avec de l'eau

Pour 3 et 4 { 2 cc d'une sol. d'orcine à 2,8%
50 mgr de AzH₂
1 cc de macération très active
de peroxydase } amener à 3,5 avec de l'eau

En comparant après 5 jours l'intensité colorante des produits 2 et 4 on voit que la richesse en orcéine est beaucoup plus grande en 4 qu'en 2 (plus que le double). Ce résultat a donc été obtenu grâce à la peroxydase.

Lorsqu'on chauffe la peroxydase pendant 5 à 6 minutes à la température de 100° avant de l'ajouter à la solution ammoniacale d'orcine en 4, on n'observe pas d'accélération dans la formation d'orcéine. C'est donc bien la peroxydase qui est l'agent actif de la transformation en matière colorante.

Pour avoir une idée de la marche de l'oxydation dans mes diverses expériences, j'ai mesuré au cours de celles-ci le volume d'oxygène absorbé; c'est ainsi que j'ai vu que dans l'expérience 1, il y a de 8 à 9 fois plus d'oxygène absorbé que dans 2, dans l'espace de 48 heures. Dans les expériences 3 et 4, on observe un écart très voisin et dans le même sens, mais grâce à la peroxydase, la proportion d'oxygène absorbé est généralement plus élevée.

Il ressort de ces faits que la quantité d'oxygène fixé dans les expériences 2 et 4 est bien moins considérable que dans les expériences 1 et 3; or c'est dans 2 et 4 qu'on observe la formation de matière colorante.

¹ On pourra facilement répéter mes expériences en opérant pour 1 et 3 dans un ballon à fond plat, pour 2 et 4 dans un petit tube à essai. On emploiera les divers produits aux doses ci-dessous:

CONCLUSION

Sans vouloir entrer ici dans de longues explications au sujet du mécanisme intime de l'action combinée de l'ammoniaque, de l'oxygène et de la peroxydase sur l'orcine, on peut affirmer que *dans les solutions étendues d'orcine c'est une oxydation lente par l'ammoniaque qui est la condition première de la formation d'orcéine.* Lorsque sur cette action vient se greffer l'influence accélératrice de la peroxydase, celle-ci s'exerce bien plus par la formation de matière colorante que par une augmentation de l'oxygène absorbé.

Les faits que je viens de mettre en lumière permettront peut-être de réaliser quelques progrès dans l'industrie de l'orseille.

THE PERMANENCY OF GOLD-TONED SILVER PRINTS

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Some twenty years ago, the photographic literature was considerably concerned with the permanency of silver prints. About that period, the time-honored albumen-silver process began to see a rival in so-called emulsion papers, made with silver salts and gelatine, or collodion, and there was a strong controversy as to whether the newer processes would give permanent prints or not. There existed two extreme camps; one which declared that neither gelatine nor collodion silver papers could produce anything but prints which were liable to fade.

The other extreme camp advocated the use of collodion silver paper and gelatine silver printing-out papers, under all conditions, and hesitated not to recommend the so-called combined gold toning and fixing bath.

This discussion was kept up on both sides of the Atlantic, and much verbiage made up for scant or unmethodical observations. These observations, on account of the novelty of the processes, were necessarily restricted to very brief periods. If failures of permanency were reported on one side, they were attributed to bad washing, bad fixing, or careless manipulation, or again, if others produced satisfactory results, it was immediately suggested that a longer period of observation would show fading effects. It was noteworthy that in such countries as England, Germany and France, where the annual extreme conditions of temperature and moisture in the air vary relatively little, combined bath-toning seemed to have many optimistic supporters, who referred to prints thus toned, which had kept very well for years. But it frequently happened that the same prints, after being transported to the United States, deteriorated very rapidly during the sultry and hot summer months, when temperature and humidity in the atmosphere coöperate to effect chemical changes on the silver image.

In order to determine what printing processes could be considered permanent or not, and in order to establish rapidly in some measure their relative permanency, I devised a simple laboratory method which I have since published. (Method for determining the relative permanency of photographic prints, by L. H. Baekeland, Fifth International Congress of Applied Chemistry, Berlin 1903, Section IX, Vol. IV, page 377.)

This method allowed me to study rapidly the subject without having to wait for the exasperating "test of time." On the strength of the indications of this method, I rejected the combined bath processes, and I insisted that permanent prints could be made either on collodion—or on gelatine—emulsion papers, provided the prints were toned in a separate neutral or slightly alkaline gold bath, made with gold-chloride rendered slightly alkaline by means of bicarbonate of sodium and acetate of sodium, and fixed separately in neutral hypo.

This separate bath treatment, in neutral or alkaline gold-chloride solution, was rather trying on gelatine emulsion papers, especially in summer, and therefore, I devised a gelatine paper of which the film was insoluble in warm water and could be treated in baths containing no hardening substances.

This effect was obtained by the judicious use of certain organic chromium salts, for instance acetate and monochloracetate of chromium, in conjunction with the usual silver salts.

On the strength of my testing methods, I foretold that prints thus toned in separate baths would remain permanent.

Some such prints, made on gelatine-emulsion printing-out paper and toned in a gold-bath containing enough acetate of sodium and bicarbonate of sodium to make it slightly alkaline, made in the summer of 1894, have been now steadily under observation in a place where they were submitted continuously to the action of light and to our extreme variable climatic conditions; at the end of this relatively long period, they have not undergone any important change in appearance. In fact, they appear as fresh and brilliant as the day they were made. I do not attribute this result to the organic chromium salts, but simply to the careful method of toning, followed by good fixing in a neutral hypo bath, and by proper washing.

LA SPECTOGRAPHIE ET SES APPLICATIONS

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I

Pendant longtemps l' étude du spectre s'est limitée à la partie visible; malgré le peu d'étendue de cette région on sait combien furent fructueux les résultats qu'on put en tirer.

Le spectre observable dans un spectroscope ordinaire s'étend de 0.67μ à 0.39μ ; à partir de cette dernière longueur d'onde qui limite la région violette visible, commence l'ultra violet.

A première vue, cette partie invisible du spectre, encore moins étendue que la région visible peut sembler peu intéressante. Il n'en est rien, et les très remarquables travaux de M. M. Berthelot et Gaudechon viennent de lui donner une importance insoupçonnée.

Au point de vue spectroscopique pur, la région ultra violette présente encore d'autres avantages.

La dispersion de toutes les substances réfrigentes augmente on le sait très rapidement lorsqu'on s'adresse aux radiations de courte longueur d'onde. On peut poser approximativement que la dispersion croît en raison inverse du carré de la longueur d'onde.

Il en résulte donc que l'étalement dans l'ultra violet devient considérable ce qui présente un très gros intérêt étant donné la multiplicité des lignes spectrales d'un grand nombre de métaux.

Mais ce qui rend surtout avantageux l'examen de la région ultra violette, c'est la possibilité que l'on a de la photographier et d'enregistrer ainsi avec ses détails les plus délicats le spectre d'un corps.

Le cliché obtenu qui est 4 où 5 fois plus étendu que la partie visible offre en outre l'avantage de permettre l'identification très facile de ses raies.

Pour cela, les spectrographes sont disposés de manière à permettre de photographier côté à côté, et sur une même plaque ou pellicule, le spectre inconnu étudié et celui du fer pris géné-

ralement comme spectre étalon par la plupart des savants. Les nombreuses raies données par ce métal ont été soigneusement identifiées par MM. Buisson et Fabry qui ont donné la longueur d'onde de la plupart des 1500 raies photographiables de ce métal.

L'alliage Plomb Cadmium est également employé dans ce but, ses raies très uniformément distribuées sont également très bien connues et quelques unes se trouvent dans la partie photographiable la plus extrême.

On conçoit donc qu'il soit possible d'identifier les raies inconnues qui se trouvent encadrées toujours entre les raies très rapprochées du spectre étalon.

On se sert pour cela d'une sorte de petite machine à diviser dite "Machine à mesurer" et dont nous donnerons plus loin une figure.

II

Ces grands avantages ne vont pas sans quelques difficultés heureusement surmontées aujourd'hui: la seule substance d'un emploi pratique possible, pour la construction des prismes et lentilles des spectrographes est le Quartz, à cause de sa transparence extrême pour l'ultra violet. Cette transparence s'étend précisément jusqu'aux radiations de longueur d'onde 0. 19 μ ou l'air lui-même commence à produire une absorption.

Mais comme il est à peu près impossible d'achromatiser les lentilles du collimateur et de la chambre noire, les divers foyers colorés constituantes raies ont des longueurs variables, et la "diacaustique" ou image spectrale est assez courbe et se trouve inclinée d'environ 63° sur l'axe de la chambre noire. Le moindre défaut de mise au point se trouve ainsi amplifié par cette grande inclinaison et les déréglages de l'instrument se produisent fréquemment.

J'ai réussi à supprimer toutes les lentilles dans la construction d'un nouveau spectrographe dont je vais décrire ici les derniers perfectionnements; ainsi que nous allons le voir, c'est le prisme qui sert à la fois à la dispersion des rayons et à la mise au point du spectre obtenu. Les avantages réalisés par cette simplification sont assez nombreux:

Citons d'abord l'inclinaison moins grande de la plaque pho-

tographique (51° au lieu de 64°); l'absence des réflexions parasites qui se produisaient dans les anciens appareils sur les lentilles du collimateur et de la lunette; une netteté uniforme dans toute l'étendue du plan focal; la diminution de la durée de la pose; un réglage facile et stable et enfin, comme conséquence de la simplicité même de l'appareil, un prix moins élevé que celui d'un spectrographe de même puissance.

Les qualités de ce nouvel appareil permettent son emploi dans les laboratoires industriels, où les recherches spectroscopiques précises peuvent être utiles, tant au point de vue des minéraux et des matières premières, que pour l'examen des métaux ou alliages obtenus. On sait quelle précision ont introduits dans ce domaine les beaux travaux de M. A. de Gramont. Comme l'a montré cet habile observateur, l'étude des raies ultimes sur le spectrogramme ne renseigne pas seulement sur la présence des métaux, mais peut même donner des indications précieuses sur la titre du métal dans l'alliage ou dans le minéral.

PRINCIPE DU SPECTROGRAPHE

La théorie très simple du nouveau prisme qui est la seule pièce optique du spectrographe FERY, fera mieux encore ressortir les avantages du système.

On sait que pour obtenir un spectre pur, il faut opérer sur un faisceau de rayons parallèles traversant un prisme au minimum de déviation. Il serait plus général de dire qu'il est seulement nécessaire d'obtenir sur toute la surface réfringente un angle d'incidence constant. Ce deuxième énoncé permet l'emploi de surfaces courbes sphériques, pour le faisceau divergent issu de la fente.

Considérons, en effet (fig. 1) la surface réfringente sphérique P C, dont le centre est en A; il est facile de trouver un point C, tel que les angles d'incidence A P C et A Q C soient égaux¹.

¹ Le degré d'approximation avec lequel cette égalité des angles est réalisée pour tous les autres points de la surface est exactement le même que dans le réseau concave de Rowland. Théoriquement, la surface réfringente devrait être une portion de spirale logarithmique $r=a e^{bt}$. L'aberration de ce fait est tout à fait négligeable pour un prisme de 50 m/m de côté et 100 c/m de foyer utilisé dans l'appareil.

5218

4063

3274
3247

2724

2370

2199

FIG. A.

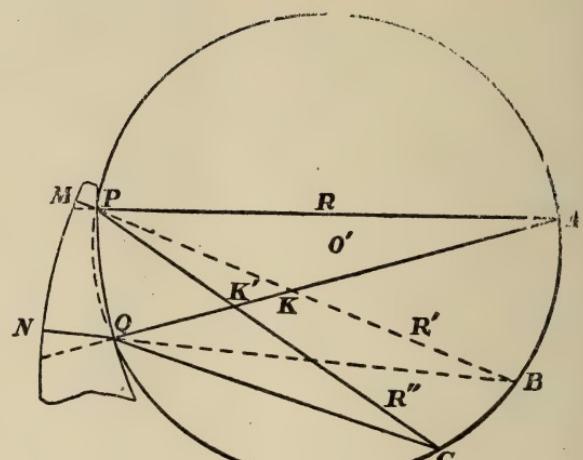


FIG. 1.

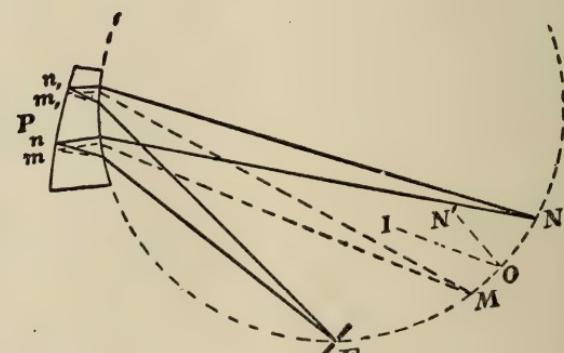


FIG. 2.

Après réfraction on obtiendra également pour ces deux rayons une déviation égale, et ces rayons sembleront provenir du point virtuel B.

C'est ce point qui est choisi comme centre de la seconde surface réfringente, de sorte que les rayons réfractés P M et Q N tombent normalement sur la face courbe d'émergence M N qui est rendue réfléchissante. La radiation monochromatique considérée reviendrait donc former, par auto-collimation, un foyer exact sur la fente C.

On voit facilement que les points A B C Q et P sont placés sur un même cercle construit sur le rayon R de la face d'entrée pris comme diamètre.

Si on emploie une radiation hétérochrome pour éclairer la fente, on obtient un spectre, et la diacaustique épouse le cercle passant par les centres de courbure de surface du prisme et la surface d'incidence elle-même.

La figure 2 montre l'effet de la dispersion sur deux radiations extrêmes, dont les foyers se font en M et N, la fente ayant été rapprochée du prisme pour éviter que le spectre ne vienne s'y superposer.

C'est donc en M N qu'on disposera le châssis renfermant la plaque photographique. L'angle I O N', mesurant la direction moyenne du faisceau I O par rapport à la normale N' O, est inférieur à 51°.

COMPOSITION DU SPECTROGRAPHE

La figure 3 montre l'appareil réalisé sur ce principe et dont le couvercle a été enlevé: un socle massif de fonte pesant environ 50 kilogrammes supporte à une de ses extrémités le prisme P qui est muni de tous les réglages nécessaires à son orientation, le support du prisme peut coulisser également dans une glissière pour une mise au point grossière; à l'autre extrémité du bâti, et faisant corps avec lui, est le porte-châssis solidaire du support de la fente; c'est par le déplacement longitudinal de cette dernière que la mise au point est achevée.

La fente C (fig. 4) dont les couteaux en nickel ont de longues parties ajustées pour que leur déplacement reste toujours ri-

goureusement parallèle, sont rapprochés par un ressort et écartés par une vis portant un tambour divisé en 200 ièmes de m/m. Cette disposition a l'avantage sur celle inverse d'empêcher l'écrasement des arêtes de la fente lorsque l'on serre trop la vis. Cette fente comporte, en outre, un mouvement de rotation autour de l'axe du tube qui la supporte, afin d'être amenée à être parallèle à l'arête du prisme, elle peut être bloquée en position après réglage.

La mise au point s'effectue sur la partie visible du spectre, et le porte-châssis I (fig. 4) peut pivoter autour d'un axe passant

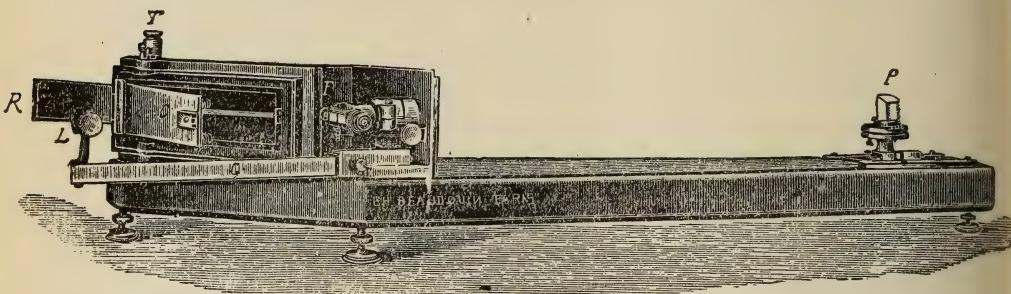


FIG. 3.

par cette région (extrémité gauche); on peut donc, en prenant quelques photographies sur la même plaque et sous des orientations différentes, faire varier la mise au point dans l'ultraviolet sans altérer la netteté de la partie visible, le réglage est ainsi obtenu rapidement.

Un tambour, visible sur la figure 3 déplace un écran intérieur muni d'une fenêtre horizontale H (fig. 4) qui limite à 4 m/m la largeur de la plaque exposée. Un tour de tambour correspond exactement à 4 m/m, de sorte que les différentes poses successives donnent des spectres tangents ayant 4 m/m de largeur, sur 215 m/m de longueur. On peut ainsi obtenir 6 poses sur une plaque 6/24 facile à découper dans le format industriel 18/24.

Le châssis porte-plaque est entièrement métallique, il porte un gabarit cylindrique du rayon de courbures de la surface focale et sur lequel la plaque vient se cintrer.

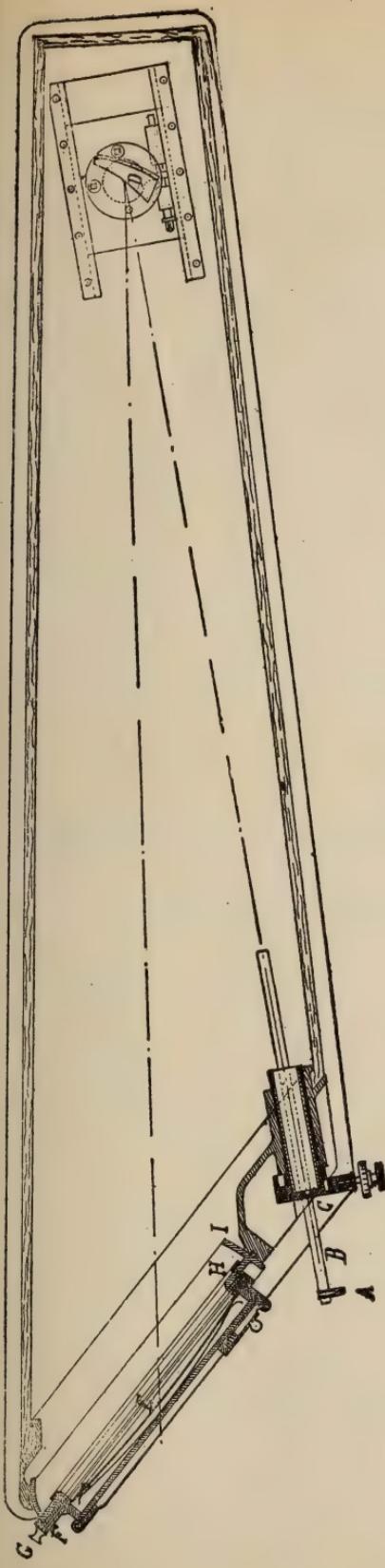


FIG. 4.

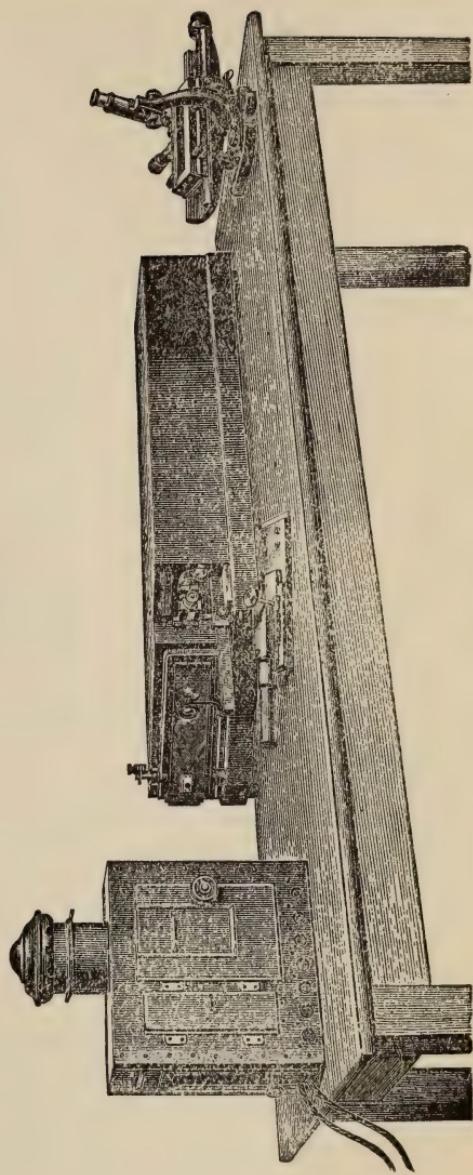


FIG. 5.

L'éclairage de la fente est obtenu au moyen d'une petite lentille cylindro-sphérique A (fig.4) donnant sur la fente une image linéaire de la source (arc ou étincelle). (Le temps de pose avec l'étincelle fournie par une bobine donnant 15 c/m d'étincelle et munie de jarres et selfs convenables a été trouvé être de 30 secondes environ). La glissière B qui porte la lentille d'éclairage coulisse dans la direction même du prisme, ce qui assure l'éclairage de ce dernier dès que l'image de la source tombe sur la fente. Une fenêtre percée à l'extrémité du couvercle permet d'ailleurs de s'assurer facilement si cette condition est remplie.

La figure 4 est une section horizontale de l'appareil par un plan passant par l'axe du tube supportant la fente: D est le prisme monté sur un support à glissière; C la fente éclairée par la lentille cylindrosphérique en quartz A; B est la glissière supportant la lentille; H l'écran limitant les spectres successifs et G le volet de fermeture du châssis.

Dimensions:

Prisme, largeur de la surface extérieure 58 m/m, hauteur 50 m/m.

Distance de la face du prisme au centre de la plaque photographique 1.080 m/m.

| | |
|---|----------|
| Plaque photographique | 24/6 c/m |
| Longueur totale de l'appareil | 1.32 m |
| Plus grande largeur | 0.32 m |
| Plus petite largeur | 0.19 m |
| Hauteur totale | 0.23 m |

Le spectre de 215 m/m de long s'étend de 1 = 6.700 U. A. à 2.200 U. A.

Il peut être important d'utiliser cet appareil comme spectroscopie, soit pour repérer des raies dans la région visible, soit pour examiner rapidement le spectre lumineux et voir s'il est utile de tirer une épreuve photographique.

La longueur du spectre visible est de 45 m/m, mais la netteté est telle que l'image aérienne peut supporter un grossissement de 20 diamètres. Un petit microscope coudé, porté par une

plaqué métallique qu'on peut glisser à la place du châssis photographique permet de faire cet examen dans d'excellentes conditions. Un vernier entraîné par le microscope et donnant 0/50^e de millimètre permet de faire des pointés à environ 1 U. A.

La figure 5 donne la vue d'une machine très commode pour la mesure des spectres.

Étant donné la netteté des résultats obtenus et la précision du repérage des raies spectrales, la nouvelle méthode spectrale par enregistrement photographique s'est rapidement répandue non seulement pour les recherches de théories pure, mais aussi dans l'industrie où elle sert à l'examen des minerais à traiter, et permet de contrôler à chaque instant la fabrication.

RECENT ADVANCES IN OUR KNOWLEDGE OF COLD LIGHT

HERBERT E. IVES

No more fascinating field of research exists than that of light production by means other than high temperature. Both from the standpoint of scientific theory and from the standpoint of practical light production, the opportunities for increasing and applying our knowledge are great. On the other hand, there is scarcely any field of science in which adequate theories are so few or so unsatisfactory. The theory of light production by luminescent processes is thus in striking contrast to the Wien-Planck theory of temperature radiation.

The general characteristics of luminescence are, first, the low temperatures at which the light is produced, and second, the discontinuous spectra of such light. Conforming to these characteristics are the luminous phenomena produced by a variety of causes, in different media, and under various conditions. The usual classification is into fluorescence and phosphorescence, produced by light, cathode rays, X-rays, etc.; electro-luminescence, produced by the passage of an electric current; tribo-luminescence, brought about by friction; thermoluminescence, caused by gentle heating; and chemi-luminescence, accompanying chemical reactions, and including the interesting cases of light production by living organisms.

A very large amount of experimental work has accumulated along these lines, and no more than a brief mention of the more striking researches, with their theoretical bearing, can be here attempted.

FLUORESCENCE: By fluorescence is commonly understood the production of light possessing the characteristics of luminescence while under the influence of the exciting force, which latter may be light, cathode rays, or other form of radiant energy. Besides the general characteristics of luminescence above noted, fluorescent light has been thought to conform to Stokes' law, which

states that the emitted light is always of greater wave length than the exciting.

Among the most important recent experimental work on fluorescence must be ranked that of Wood, on sodium and other metallic vapors. By the use of improved technique, and of higher spectroscopic resolving power, the fluorescent spectrum of sodium vapor was found, when white light is employed as excitation, to be of a delicate banded structure. When, however, monochromatic excitation is used, there results not a banded but a line fluorescent spectrum. As the wave length of the exciting light is changed, different sets of line spectra appear, each forming a regular series. In these series Stokes' law is not observed, for by exciting any one line of a series by resonance all the other lines respond, indicating that the various monochromatic radiations are given out by a common system. Much information as to the nature of the radiating systems will undoubtedly follow from this work and from that now being carried on in continuation of it. Among the latter researches may be noted the remarkable experiment of changing the line resonance spectrum of iodine vapor into a band spectrum (resembling that excited by white light) by means of the presence of helium gas.

In a somewhat different field are the interesting fluorescent spectra found by Goldstein in the aromatic compounds, which exhibit peculiar changes in intensity and character with variations in the excitation and physical conditions.

Nicholas and Merritt, in an extensive series of studies, have determined the distribution of intensity in the spectra of various fluorescent substances, and the effects of temperature thereon. Their latest work, on the distribution of intensity among the narrow bands in the spectra of the uranyl compounds, shows that the envelope of these bands has a shape similar to that of the intensity distribution in the broad single emission bands of many other fluorescent substances, such as the alkaline earth sulphides. Taken in conjunction with the fact that these bands are much sharper at low temperatures (Becquerel) and broaden at high temperatures, there is here evident for the complex character of the rather common diffuse emission bands given by fluorescent and phosphorescent substances.

The chief theories of fluorescence consider it in relation to phosphorescence and will be treated here under that head.

PHOSPHORESCENCE: By phosphorescence is commonly understood a luminescence which persists after the removal of the excitation period. Frequently it is considered as differing from fluorescence in this respect alone and the one is held to graduate insensibly into the other. Certain substances which on ordinary examination appear to be merely fluorescent are found on examination with the phosphoroscope to exhibit a phosphorescence of very short duration. Often the duration of this phosphorescence may be increased by lowering the temperature.

Attention must here be directed chiefly to two investigators and their theories, and to the work which has been done by them or inspired by them,—Kowalski and Lenard. The theory advanced by Kowalski calls for two systems of electron groupings, called electronogens and luminophors. The first expel electrons under the influence of light; the second have an internal energy closely approaching the critical value at which explosive action takes place in accordance with the ideas of J. J. Thomson. Under the influence of light the electronogens expel electrons which carry additional energy to the luminophors, destroy their equilibrium and so cause disintegration and emission of light.

Recent experimental work by Kowalski on organic compounds at low temperatures has resulted in the separation of two processes, one of which decays with great rapidity on the removal of the excitation, the other much more slowly. The two processes have different spectra. These results are apparently more in accord with the theory of Lenard, which follows.

Lenard has directed his study to the alkaline earth sulphides, of which Balmain's paint (calcium sulphide) and sidot blende (zinc sulphide) are examples. Through an exhaustive investigation in conjunction with Klatt, he has definitely determined the composition of these sulphides. The constitution of a "phosphor" is three-fold: first, an active metal, present in very small quantity; second, an alkaline earth sulphide; third, a flux. Having reduced the preparation of the phosphors to a science, Lenard has conducted noteworthy investigations on the properties and behavior of these substances under different excitation

and conditions. Each phosphorescent spectral band has been found to have three phases—a lower momentary phase, at low temperatures; a permanent phase; and an upper temporary phase at high temperatures. The characteristics of the permanent phase are that first, it gives lasting phosphorescence, and second, it is caused chiefly through excitation by light at several isolated spectral regions. The temporary phases are excited by a large range of short wave-length radiation, and are of excessively short duration of phosphorescence. The various bands have their permanent phases at different temperatures.

To explain these phenomena, Lenard has formulated a very striking theory. He considers the action of light to be the photo-electric action, that is, the tearing off of electrons from the active metal by the resonance action of light. These electrons are then captured by the surrounding sulphur atoms. Some are released at once, others are stored and only gradually returned. The (photo-electric) electrons on their return, vibrating with every decreasing amplitude and period, set in motion, by resonance, at a certain period in their decreasing swing, another set of electrons in the metal atoms, the latter called "emission electrons." It is the vibrations of the emission electrons that cause the visible light, of greater wave length than the exciting (Stokes' law). The extinguishing action of infra-red radiation is attributed to the fact that the free period of the captured metal electrons is such as to respond to the longer wave excitation. The complex molecule is set into vibration and gives up its metal electrons sooner than it otherwise would.

Some deductions from this theory have met with strong confirmation. It has been found, for instance, that the relative wave lengths of the permanent excitation regions for the same active metal may be derived from the dielectric constant of the alkaline earth sulphide. The theory calls as well for a number of bands not to exceed the number of valence electrons, that is, four, and although Pauli has recently found both ultra-violet and infra-red phosphorescent bands this number is not exceeded.

An interesting contribution to this theory has recently been made by Pohl. Lindemann has discovered that the wave length at which metals respond to the selective photo-electric effect

may be calculated from the atomic volume and valency of the metal, on the assumption of a planetary system obeying Kepler's laws. Pohl calls attention to the fact that the wave lengths which excite the permanent phase of phosphorescence are in the ratio to each other given by Lindemann's relationship, in which the successive valences 4, 3, 2, are substituted, thus supporting Lenard's view that we have here a case of the selective photo-electric effect.

ELECTRO-LUMINESCENCE: The production of light by the passage of an electric current through a rarefied gas belongs in the category of luminescent phenomena, although the chief study has been from the electrical rather than the light standpoint. The past few years have, however, marked the commercial development of electro-luminescent devices, prominent among which are the Moore tubes, containing either carbon dioxide (white light) or nitrogen (yellow light). Lately tubes of Neon have been employed, noteworthy because of the low cathode drop and the large portion of the emitted energy which lies in the visible spectrum.

CHEMI-LUMINESCENCE: That light is an occasional accompaniment of chemical action, even at low temperatures, has long been known. Trautz, in a remarkably exhaustive study, has recorded some hundreds of cases of chemi-luminescence in its various forms of crystallo, tribo, and purely combination luminescence. No generalizations are possible at present beyond the observation that velocity of reaction and intensity of luminescence are approximately proportional. Some of the more intense of these reactions, such as that of pyrogallol and hydrogen peroxide, have been the subject of special investigation, but in all cases the amount of light produced was very small and difficult of study.

ORGANIC-LUMINESCENCE: More and more attention is being devoted to the study of organic luminescence, whether of bacteria, marine organisms, or the luminous worms and flying insects. In these, nature has solved the problem of light production in a manner different from that so far achieved by man. While usually the total light emitted is small, the intrinsic brilliancy is not so small as to make a similar light useless to man could he copy its mode of production.

Perhaps the most significant work done of late has been on the fire-fly. On the physical side, work by Ives and Coblenz has shown the spectrum of the emitted light to consist of a narrow band in the visible region, unaccompanied by an emission in all the ultra-violet and infra-red which could be studied by photography or phosphor photography, and with strong evidence that such invisible radiation cannot exist. Nor does the radiation possess any of the characteristics of true phosphorescence, such as dependence on light for excitation, or susceptibility to extinction by infra-red.

Interesting work by Kastle and McDermot on the chemical side has shown that the light giving power of the insects is affected by many chemical reagents in a marked manner. They find the necessary conditions for the production of light to be the presence of oxygen and water. Perhaps the most important result of their work has been the discovery that the dry powdered abdominal material of the insects will give out light when moistened for as much as two years after the insect is dead, proving the emission of light to be a chemical phenomenon not dependent on life.

RECENT PROGRESS IN PHOTOMETRY

HERBERT E. IVES

The science of photometry has received great impetus within the last few years, partly owing to the phenomenal growth of that branch of applied science known as Illuminating Engineering. This progress is also partly a reflection of the large amount of work being done in the field of physical optics and in the physiology and psychology of vision. The influence of the former science is seen in new types of instruments, of the latter sciences in the methods and interpretation of results.

PHOTOMETRIC METHOD

Heterochromatic Photometry

Probably the largest single problem in photometry has for many years been the evaluation of the brightness of lights of different colors. Until the recent rapid multiplication of kinds and colors of light sources this problem was of more scientific than practical importance. It has lately assumed industrial importance as well, and much work has been done on it.

There are several difficulties in making brightness measurements on lights of different colors. In the first place the two quantities under comparison are ineradicably different in character, and the eye, which equates but does not appraise, is for this an inadequate instrument. It must try to separate out the quality of brightness from that of hue and must then perform the equating operation.

Making a photometric match subject to such difficulties is an operation which at first trial often appears impossible. Even if by practice the observer arrives at a criterion, this may change as his memory of previous settings fails him, and when two observers differ—as they usually do—there is no means of deciding which is “right.” While some investigators have made

brightness measurements by the simple comparison of illuminated surface (the "equality of brightness" method, as it is called), it is generally agreed that such measurements are subject to great uncertainties. There has long been the need for some method of photometry which shall make possible definite, dependable, reproducible measurements.

But it must always be remembered that even the adoption of such photometric method (if it exist) does not solve all difficulties. Different observers differ in their color vision, even without being so abnormal as to be called color-blind. Some procedure which will record only the values applying to a normal or average eye is desirable; it is, in fact, essential. For the differences between different observers may easily cause discrepancies between their measurements far greater than the errors of measurement themselves.

A still further source of confusion in heterochromatic photometry lies in the physiological peculiarities of the eye. As the order of illumination changes the relative brightness of colors also changes (Purkinje effect). As we vary the area and portion of retinal surface which is excited the relative brightness of colors changes due partly to the pigmentation of the retina. What conditions shall hold and what conventions shall be adopted in order to best minimize the importance of these subjective factors must form the subject of photometric research and legislation.

Several photometric methods have been used for heterochromatic photometry—visual acuity, persistence of vision, equality of brightness and, lately, the flicker photometer. Until recently no data have been forthcoming as to the behaviour of these methods under various conditions, or their relative sensibility, or even the relationship between the criteria of each.

An extensive investigation recently completed by H. E. Ives places this whole question upon a definite footing. The four photometric methods were studied side by side under a series of different conditions of illumination and size of photometer field. As a result of this study it appears that the flicker photometer possesses the maximum number of attributes of a good method of measurement. It greatly excels the others in definiteness,

sensibility and the reproducibility of its readings. At low illuminations it shows a reversed Purkine effect, but at ordinary working illumination—in the neighborhood of 25 meter-candles—it gives the same results as are obtained by a very large number of independent measurements made by the equality of brightness method. The behaviour of this photometer under all tests speaks decisively in favor of its adoption for this kind of light measurement.

If the flicker photometer be adopted, to be used under the standard conditions of illumination, a satisfactory solution of this problem is attained. Because of individual variation in color vision, such photometry should be restricted to the standardizing laboratory, from which secondary standards or correcting colored glasses may be issued, either each measured by many observers, or else the measurements in each corrected to normal from a knowledge of the observer's spectral luminosity curve in relation to the average curve. The investigation above quoted embodies the mean luminosity of a large number of observers for use just suggested. By using such secondary standards, all practical photometry could be reduced to the measurement of lights of the same color, for which all eyes, normal or color-blind, are fitted at any practical illumination.

COLOR MEASUREMENTS

The importance of color in illumination has prompted measurements of color both by the spectrophotometer and by three-color mixture. These have shown in quantitative form the wide divergence of most artificial illuminants from daylight color, their common defect being a yellow tinge or deficiency in blue. One outcome of these measurements has been the imitation of daylight by the utilization of absorbing media in connection with some of the ordinary illuminants.

USEFUL QUALITIES OF LIGHT

A noteworthy development in photometry is its change from a strictly geometrical science to one involving physiological characteristics. This is illustrated by the complexity of the

problem of heterochromatic photometry as contrasted with the simplicity of photometry with lights of similar color. It is illustrated again in the case of color measurement. Into color measurement enters another basis of evaluation—that of usefulness for certain purposes. The determination of the characteristics of a light good for color discrimination and color matching is one subject of study in the problem of color measurement. More definitely utilitarian are certain investigations which have been carried on, notably by Dr. Louis Bell, on the detail-revealing power of different kinds of light. These investigations show a very great advantage in favor of monochromatic light, because of the chromatic aberration of the eye. On the other hand where it is a case of color discrimination, light as far from monochromatic as possible is called for. Increasing attention may be expected to be given to the question of the availability of illumination for different purposes, leading finally to the use of "quality factors" to be applied to the brightness measurements where other properties than mere intensity take on significance.

INSTRUMENTS OF PHOTOMETRY

Simple Photometers

Several new forms of photometer, of the equality, contrast and flicker types, have all three appeared within recent years. Few of these which have achieved prominence have been dictated by any new theories or photometric discoveries. Among those that are really new are the binocular photometers of two different forms, suggested by the work of Stiegler, which indicated that a greater sensibility is attainable by the use of two eyes than of one.

Photometers for Special Purposes

Good practice in photometry is dictating more and more the comparison of light sources by the measurement of total light flux in place of horizontal or other partial basis. The most important aid to the practice has been the development of the integrating sphere, chiefly due to Ulbrich, consisting of a hollow sphere of diffusely reflecting surface in which the light to be measured is suspended.

In the electric lamp industry the growing practice of rating lamps at a certain efficiency has brought into being several instruments for measuring watts per candle and for setting lamps at a desired specific consumption.

Accessories

In connection with auxiliary photometric apparatus may be mentioned the several uses found for opaque line gratings, notably their use singly as strictly neutral tint absorbing screens; combined in pairs to form variable absorption screens, and crossed to make a very perfect test object for visual acuity (Ives).

Substitutes for the Eye

Almost since the beginning of photometry investigators have sought some form of sensitive radiometer which might take the place of the eye. With the realization of the individual differences in color sensitiveness the idea of a visual substitute, sensitive to radiation in the same manner as the average eye, has come still more to the fore. Féry has used this idea in a direct reading photometer, consisting of a radiomicrometer before which is placed an absorbing screen of nickel salts. Houston has more recently proposed a screen of copper sulphate and potassium bichromate to approximate more closely the visual luminosity curve.

Selenium, because of its high sensitiveness to light, has been much experimented with. Recent work by Pfund, however, has shown a variation in the law of response with the wave length of the exciting light, of such character that only by working under certain previously empirically determined conditions does it appear possible to use the selenium cell for light measurement.

More and more attention is being paid to the photo-electric cell composed of alkali metals. The photo-electric effect appears to be directly proportional to the illumination, and so sensitive is this cell that measurements of the faint light of phosphorescence can be made with it. By so screening it as to make its color sensitiveness that of an average eye, a most promising photometric possibility lies ahead.

PHOTOMETRIC NOMENCLATURE AND STANDARDS

Progress in the definition of photometric quantities is slowly being made through the work of the Illuminating Engineering Societies and Committees here and abroad. Several new points of view and terms have made their appearance. *Luminous flux* is taking the place of *luminous intensity* as the fundamental quantity. *Luminous efficiency*, a term formerly appropriated or the merely physical ratio of "visible" to total radiation, is being evaluated more and more on the basis of the light of maximum possible efficiency, namely, monochromatic yellow green light. When so expressed, luminous efficiencies are directly proportional to lumens per watt, or to lumens per b. t. u. per hour, which is proper for a quantity purporting to be an efficiency.

Another new term is *daylight efficiency*, based on the loss in intensity caused by absorbing the excessive radiation in a light source to reduce it to daylight color.

In the realm of units great practical progress was made when England, France and the United States jointly adopted a common unit of candle power, sometimes called the International Candle.

Photometric standards have received considerable attention, from both the practical and the theoretical standpoint. The present so-called primary standards, such as the Pentane lamp, have been the subject of painstaking study which has resulted in increased knowledge of their peculiarities and in improvement of construction.

Perhaps the most important theoretical advances in the question of photometric standards have been the proposals to connect the light unit with the c. g. s. system and thereby produce as nearly as may be a true fundamental standard. These recommendations all take the form of measuring light as radiant energy properly weighted to correspond with its luminous value. Strache proposes to accomplish this by diaphragming the spectrum according to the visual luminosity curve; Houston suggests the use of a special absorbing screen; Ives proposes the measurement in both light and energy units of a selected monochromatic radiation. His proposal brings in as well the rational evaluation of luminous efficiency; in full it is that the unit of luminous flux

should be the flux from a source of maximum luminous efficiency radiating energy at the rate of one watt. This embodies the simplest possible analysis of luminous flux into its two parts, physical and physiological. The attainment of this standard is scientifically desirable and is practically dependent on the adoption of a satisfactory method of heterochromatic photometry and on the refinement of our means of measuring radiant energy.

THE PRESENT CONDITION OF COLOR PHOTOGRAPHY

HERBERT E. IVES

The past five years have been noteworthy in the history of photography as marking the appearance of processes of color photography which have, in the fullest sense, been practicable and have been used extensively by the professional and the amateur photographer. While there is yet to be seen the simply produced print on paper which to the popular mind can alone deserve the name of color photograph, still pictures are now tolerably common which need neither an instrument to render them visible, nor delicately arranged conditions of viewing. It must be said, however, that in correctness of color rendering, no advance has been made on the three-color reproductions shown by F. E. Ives twenty years ago in the Kromskop, nor over some of the most perfect examples of the Lippmann process of almost the same age. Recent developments have all been toward simpler or popularly more acceptable means of achieving the same result.

It will be most feasible to discuss progress in color photography after making a classification of the various methods into direct and indirect methods. (The latter again may be arranged under various sub-heads, as is done below.) Considering, now, direct methods of color photography, there is but one illustration—the Lippman or interference process. Because of extreme delicacy of manipulation, and because it is subject to disturbing influences, it has been used successfully by very few. Some work, however, has been done with it comparatively recently. H. Lehmann, Cajal and H. E. Ives have made studies of modes of preparation of the sensitive film, of the action of the different developers, and by means of sections of the film, of the action of various types of light. These have in the main confirmed the beautiful scientific theory which underlies this method. The last named investigator, by using certain slow, clean work-

ing developers, and by bleaching with mercuric oxide, has produced films containing hundreds of reflecting surfaces and possessing a resolving power sufficient to reproduce spectral colors with great purity. Lehmann has developed a special color screen for taking interference pictures, in which are three maxima of transmission whereby whites are produced by a set of laminae instead of by a diffuse deposit, which latter frequently possesses a single maximum of reflection, corresponding to the center of the sensitive region of the plate, or to green. Some substitutes have been proposed for the mercury mirror originated by Lippman, but no attempts to simplify the process in this way have encouraged many to use it. The interference process seems in fact fated to remain only a beautiful scientific demonstration.

Indirect processes of color photography are those in which the color is not produced in the picture by the action of light, but is added either by instrumental means or by colored media, such as dyes. These processes naturally fall into two classes: one, represented by the prismatic dispersion process, in which the actual spectral composition of the original color is copied; the other, those making use of the physiological characteristics of the eye, whereby colors may be reproduced subjectively by the objective mixture of others. The first processes are at present confined to several schemes originated by Lanchester and others, whereby the image of the object photographed is spread out into a large number of narrow adjacent spectra, by the combination of a prism with an opaque line grating. The positive from the negative thus obtained is then viewed through an instrument similar to the camera. The images of the narrow spectra act as templates, transmitting more or less of the spectral colors to the eye at different points on the image. Thus an exact reproduction of the acting light is obtained, and the colors are reproduced in such a manner that they appear correct to all observers no matter what their peculiarities of color vision. The necessity for using a viewing instrument and of accurately adjusting the linear spectral images to their spectra are, of course, disadvantageous from the practical or commercial standpoint.

With these brief notices of direct color photography, and

indirect by spectral analysis and synthesis, we come to those processes which have produced by far the most promising and practical results, namely, the color mixture processes, which practically reduce to various forms of the three-color process. The theory of three-color photography, first put into scientific form by Maxwell, and later developed by F. E. Ives, may be outlined as follows: By experiment on color mixture, it has been found that all colors of the spectrum may be reproduced as to hue (but not absolutely as to saturation) by mixtures of three spectral colors—a red, a green and a blue. According to the experimental work of Koenig, and the theory known as the Young-Helmholtz theory, the facts of color mixture may be represented by the assumption of three so-called primary color sensations, red, green and blue, none of which are present in full purity in the spectrum. It is, however, possible to select from the spectrum the three colors in which each of the three sensations are present with least admixture of the two others, or it is possible to select three colors which in their mixture introduce least degradation of purity, that is least admixture of white (either on the whole or in colors considered most important). Having selected three primaries conforming to the latter requirement, it is possible to obtain color mixture curves, giving the mixing proportions of these selected primaries which shall reproduce the spectral colors. If, now, three negatives are made, in each of which the distribution of photographic action through the spectrum is as given by one of the mixture curves, then these three negatives, or the positives from these, when suitably viewed by the three primary colors, and combined, will reproduce to the eye the original object. It is thus seen that the theoretical requirement is for negatives taken through screens in which all the spectral colors are transmitted in certain proportions which represent the color and luminosity values, and for the viewing of the resultant positive by three colors which are only narrow isolated portions of the spectrum. Any departure from this latter condition means the use of primaries which in their mixtures either introduce more than the minimum possible amount of white, or else restrict the hue range.

The practically exact attainment of the conditions just outlined

was actually reached in three color projection, and in instrumental synthesis in the Ives Kromkop twenty years ago, and no more perfect results have since been achieved. Recent progress in three-color photography has been along the lines of simplification of procedure, often, however, made possible by some compromise with the theoretical requirements.

The most prominent three-color processes now are those known as "screen plate," of which the Lumière Autochrome, Dufay and Warner Powrie are examples. Their common characteristics, from which the name is derived, are, first, a mosaic screen of the three taking color screen, second, the negative emulsion superposed on this screen, and, third, the necessary practice of reversing the negative, in order to secure a positive, which, lying as it does in intimate contact with the mosaic screens, owes its color to the light transmitted by the complex color screen. The color photograph is a transparency, and from the manner of its production is unique and incapable of simply copying. The same mosaic of color screens is used for viewing as for taking. This entails a compromise: the constituent colors are made less pure than they should be for viewing purposes, more pure than they should be for taking. That this compromise causes a loss in fidelity of color rendering is unquestionable. Photographs of certain pure color, such as a spectral yellow which reproduces as red, show this only too plainly. Still, as most colors in nature are far from pure, and as the eye is marvelously adaptable to changes of color scale and saturation, this compromise is much less apparent in the results than might be expected. Beautiful color photographs, chiefly taken by the Lumière process, are now comparatively frequently to be seen.

The various screen plate processes differ in their mechanical details. In the Autochrome plate the components of the screen are dyed starch grains, mixed in proper proportion to produce a gray and then strewn on the plate. In most of the other processes various lines or other geometric patterns predominate, some made by ruling processes, others—notably the Warner Powrie—made by gelatine bichromate printing and subsequent dyeing. An advantage of the linear elements in the Warner Powrie Screen is that the negative may be used for making

structureless positives by a process of parallax printing. The irregular structure of the Autochrome plate keeps more than a portion of the transmitted light from being available for contact printing on another plate, or on a bleach-out paper.

Another development of the three-color idea which has produced interesting results, and which may be expected to produce more in the future, is that of complementary color printing, either as transparencies or as prints on paper. The theory underlying this method of working is the same as before, but the different mode of approaching the problem calls for a different set of colors. Instead of adding colors to produce white, the print processes start with white and build up by successive absorption until they reach black. The colors required are minus colors; that is, the nearest approach possible to the color obtained by subtracting each of the three constituents of a three-color white, colors which shall also, when taken together, produce black. These are minus red, or peacock blue; minus green, or pink; and minus blue, or yellow. The first pictures of this sort were obtained by printing the three negatives on bichromated gelatine. After development the three prints were stained with appropriate dyes and superposed, making excellent transparencies. Recent forms of this process are due to F. E. Ives. One process originated by him has for its essential characteristic the use of bichromated fish glue for the printing surface, whereby very shallow reliefs can be obtained. A later process uses gelatine bromide plates into which a quantity of yellow dyes is incorporated, which again serves the purpose of keeping the relief shallow, so that the soaking up of dye-stuff can be accurately controlled.

Two processes carry three-color printing to the form of prints on paper. These are the Koenig Pinatype process and the Sanger Sheppard imbibition process. These both make prints in gelatine, which are transferred by squeezing to a gelatine-faced or blotter-like paper.

Another printing process of great interest is the bleach-out process, known as Uto. The central idea of this is the use of a paper coated with a mixture of three dyes of minus color which, together, produce black. Each dye has the property of being

faded by its complementary color of light. Consequently, when exposed to a colored image all colors from black to white (complete fading) are attainable. The technical difficulties in the way of this clever idea are many, but a paper has actually been produced upon which prints from color transparencies have been made. At present, however, this process is not a serious rival to the screen plate.

Various cameras for the production of three-color negatives continue to be devised, but their details involve no strikingly new departures other than what may be termed mechanical ones. The use of the screen plate has led attention away from special cameras, but the possible development of improved three-color print processes may direct the ingenuity of inventors back to the problem of securing three negatives from one point of view in some simple and compact camera.

THE RATE OF RUSTING OF IRON AND STEEL

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An editorial review of chemical progress in 1911 says:—¹

"The rusting of iron has received its usual amount of study and controversy, but the question remains as ragged and dubious as it has been for years. Part of the difficulty arises from some of the investigators falling in love with a neat, trim, complete theory, blinding their eyes to its defects, and rejecting the contributions of other workers who do not worship their own idol."

In spite of the vast amount of study which has been given this subject, it is a regrettable fact that there is but a limited amount of information and data available as bearing upon the practical phases of the question. The painstaking and detailed work which has been devoted to proving or disproving a theory that carbonic acid is the cause of rusting is illustrated by the fact that one of the prominent workers in this field asserts that in spite of boiling and other methods of purifying there still adhered to the inner walls of a glass vessel in which corrosion tests were made enough CO₂ from the glass blower's breath to make the results of tests of doubtful value. On the other hand the controversy on the intensely practical question as to the relative durability of iron and steel is still unsettled; there is no reliable information as to how durability is dependent upon purity and as to the quantitative influence of various impurities. There are no standard methods of testing, by means of which the corrosion determinations made by one investigator may be compared with those made by another.

For a number of years experimental work has been carried on in the Chemical Engineering Laboratories of the University of Wisconsin on various phases of iron corrosion, and the purpose of this paper is to present some of these results as far as they

¹ The Engineer (London) Jan. 12, 1912.

deal with commercial forms of iron and steel. Various grades of commercial materials were subjected to corrosion tests during 1910 and 1911, and in presenting these results the purpose is not to draw an accurate comparison of the relative merits of various commercial materials at present available, but rather to give some data on testing methods. In view of marked advances which have recently been made the samples which were selected early in 1909 probably do not include representative samples of some of the high purity materials at present available.

No attempt is made to classify the results in accord with any theory, but rather to submit them in such manner that they may serve as a record containing some information of general usefulness, and to which results of further measurements which are under way may be compared.

While appreciating the limitations upon corrosion data as generally submitted, and while desiring to make our tests standard as far as possible, we must recognize serious limitations on our own results—limitations due partly to lack of foresight and partly to lack of facilities, time and financial resources.

Samples were prepared from six different classes of materials as representative of the range of materials obtainable on the market. These comprise several grades of open hearth iron of high chemical purity, Swedish iron, open hearth mild steel, open hearth mild steel subjected to special hot working process, Bessemer rail steel, and gray cast iron. Some of these materials were chosen both from bar and sheet stock.

The list of materials thus chosen comprise twelve in number, and six samples of each were prepared for and subjected to various corrosion tests, there being 72 test specimens in all.

The twelve materials are described in the following lists:

1. Open hearth high purity iron from bar stock—Samples 1" x 2" x $\frac{1}{2}$ " ground to smooth surface on emery disc.
2. Open hearth high purity iron—Samples 1" x 2" x $\frac{1}{4}$ " ground to smooth surface.
3. Open hearth high purity iron—Samples 3" x 3" from 16 gauge sheet. Samples were used with black annealing scale.
4. Same as 3, but ground smooth on emery disc to remove scale.

5. Swedish wrought iron—Samples 1" x 2" x $\frac{1}{2}$ "—ground smooth.

6. Open hearth steel—from plate stock—Samples 1" x 2" x $\frac{1}{2}$ "—taken as representative of good quality low carbon steel of the better grade used in boiler plate.

7. Open hearth steel sheet—16 gauge—Samples 3" x 3" with annealing scale. From designation by the manufacturer it is representative of very mild, annealed, high grade open hearth product.

8. Same as No. 7, but with scale removed and surface ground smooth.

9. Open hearth special sheet steel, 20 gauge, samples 3" x 3"—with annealing scale. Upon representation it is given as a special steel by reason of a mechanical treatment of the ingot during working down with the idea of eliminating surface heterogeneity and blow holes.

10. Same as No. 9—but with scale removed and surface ground smooth.

11. Bessemer steel—samples 1" x 2" x $\frac{1}{2}$ "—cut from the flange of a steel rail—Analysis not determined, but may be taken as representative of material having carbon content of .50 to .60.

12. Cast Iron—Samples 1" x 2" x $\frac{1}{2}$ " cut from a medium grained gray iron casting. Analysis not determined, but representative of average iron casting except that the scale or surface chill has been removed.

Six samples of each of the above listed materials were subjected to tests for corrosion; these are indicated by a, b, c, d, e and f respectively—a, b and c were exposed to the weather conditions on the roof of the Chemical Engineering building at the University of Wisconsin, and d, e and f were placed at the ventilator outlet on the roof of the Chemistry Building, where together with the weathering conditions additional corrosive action was exerted by the gaseous fumes from a chemical laboratory. It is believed that in the former case we have typical atmospheric corrosive conditions uninfluenced by smoke and fume, while in the latter case the atmospheric corrosion is considerably aggravated by fume. The former will be designated as "atmospheric corrosion," and the latter as "fume corrosion."

The fume corrosion was not, however, excessively severe, since the ventilating fan discharged the heated air at a high velocity with conditions favorable for the rapid drying of specimens after wetting from atmospheric conditions.

All samples were ground or polished to a uniformly smooth surface on a fine emery disc. However with the sheet material, duplicate sets were exposed without removal of the rolling or annealing scale. The bar samples were set in woodracks, and the sheet samples suspended in frames, all edge up; the racks were built to allow for as good drainage as possible. All specimens were first exposed on December 22, 1910, after weighing. On March 8, 1911, one of each of the three making up the various sets, was taken in, the rust was removed with ammonium citrate solution, and the loss determined. These samples were then exposed (without altering the surface conditions) a second time, on March 8, 1911. On May 21, 1911, the above mentioned samples, together with one of each set which had been out for the total period from December 22, 1910, to May 21, 1911, were taken in, and the amount of corrosion determined.

All of these specimens were then ground to a smooth finish, weighed and subjected to 20 percent sulphuric acid corrosion for one hour, according to the specifications suggested by the American Society for Testing Materials. This loss was then determined. Finally, after regrinding and weighing, the bar samples were again exposed to the previous weathering conditions on June 1, 1911. The sheets were too much corroded by the acid to be available for this test. On October 18, 1911, all specimens, including three of each bar sample, and one of each sheet sample, were taken in and the corrosion loss determined.

At the completion of these tests, all of the bar samples Nos. 1, 2, 5, 6, 11 and 12 were examined as to character and depth of pitting. This character of pitting is shown photographically. The depth of pitting was determined by carefully grinding down one of the faces of each specimen, until the pit marks just disappeared, and the amount of metal thus removed was noted. To these values were added the losses by corrosion, and the sum gives a value called for convenience the "equivalent corrosion" per square inch. Then by dividing the "equivalent corrosion"

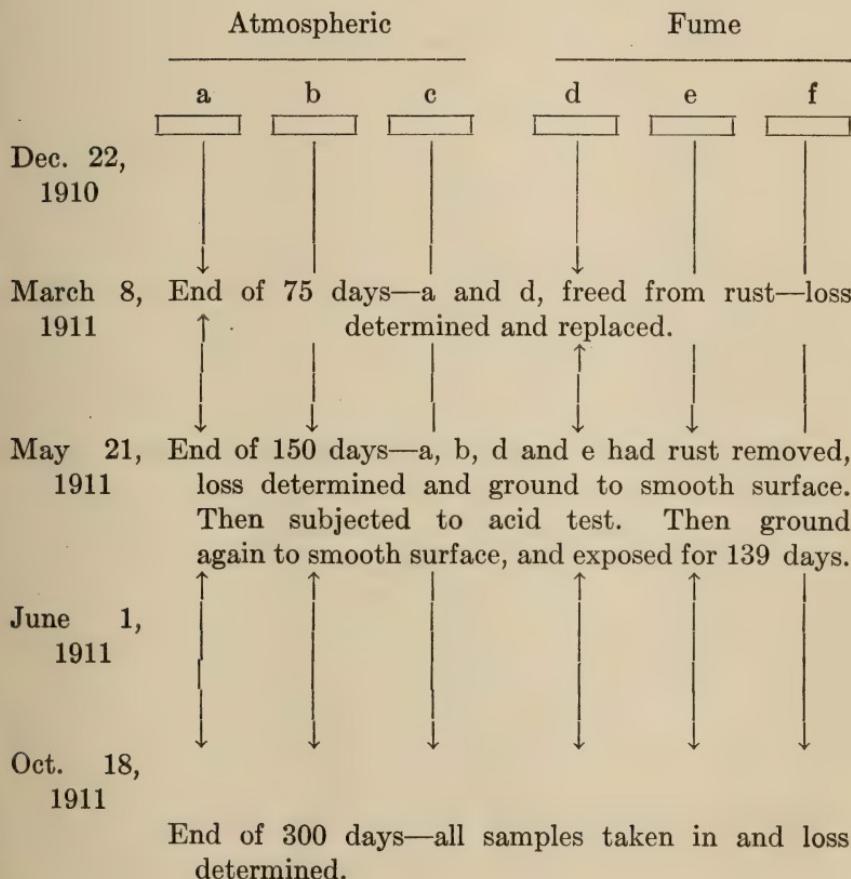
by the actual corrosion we have values which we choose to designate as the "pitting factor."

The diagram Figure 1 will illustrate perhaps somewhat more clearly the various steps through which each set of samples passed.

In making the acid tests at the end of the second period the average of a and b and of d and e were taken—it being found that close agreement existed between the two samples of each pair, though not between the two pairs.

From analysis of the data thus obtained certain conclusions

FIGURE I



of interest and of possible value may be drawn as having a bearing upon the important corrosion problem. The question which is perhaps of the greatest importance and of interest to the greatest numbers is "What is the relative durability of the various materials on the market under various corrosive conditions?" This is a question which we do not attempt to answer. Although some of the tables presented herein appear to give numerical expression to the corrodibility of various grades of materials they cannot be used as a guide since it is by no means certain that the small samples employed were truly representative of the classes of materials from which they were drawn. In fact recent microscopic analysis seems to show that in one instance at least especially inferior samples were employed in these tests. However, it is believed that the figures represent some concrete idea of the possible ranges of values which may be encountered in commercial materials as judged from the durability standpoint.

Other and more reliable conclusions can be drawn from these tests. It is shown that atmospheric corrosion depends upon the seasons of the year and upon the gaseous impurities in the air; that these impurities affect different grades of iron and steel in different degrees. Much interest attaches at the present time to the usefulness of the accelerated acid test as a means of judging the durability of the metal under various corrosive conditions, and some conclusive evidence is given to show that there is little relationship. The accelerating influence of an initial rust formation upon subsequent rusting is demonstrated. The black scale on sheet iron is shown to have little if any retarding influence upon deterioration by rusting. A peculiarity is apparently pointed out that iron after exposure to severe atmospheric corrosive conditions undergoes some deep-seated change which is evidenced by a notably decreased resistance to attack by acid. It is well known that the damage to iron by rusting is not measurable alone by the loss of weight of the metal but the depth of pitting produced by the rust is an important factor. An attempt is made to give a numerical expression to this factor.

In tables I and II the results are given as "corrosion factors," the reference unit being taken as the rate at which material No. 1 rusted per day under normal atmospheric exposure during

TABLE I
Corrosion Factors—Atmospheric Test

| Material | (a) 1st Period 75 Days Winter | (a) 2nd Period 75 Days Spring | (b) Combined Period of 150 Days | (a) 139 Day Period Summer | (b) 139 Day Period Summer | (c) Total Pe- riod of 300 Days |
|---|--|--|--|------------------------------------|------------------------------------|---|
| 1. High Purity Iron $\frac{1}{2}$ " Bar..... | 100 | 134 | 154 | 74 | 79 | 79.6 |
| 2. High Purity Iron $\frac{1}{4}$ " Bar..... | 94.5 | 109 | 143 | 67 | 59 | 83.2 |
| 3. High Purity Iron—Sheet with scale..... | 148 | 135 | 149 | | | 109 |
| 4. High Purity Iron—Sheet without scale..... | 124 | 124 | 135 | | | 90.5 |
| 5. Swedish Iron $\frac{1}{2}$ " Bar..... | 82.5 | 96 | 141 | 48.5 | 73.5 | 73.5 |
| 6. Open Hearth Steel—Boiler Plate | 97 | 123 | 135 | 48.5 | 51 | 99 |
| 7. Open Hearth Steel—Sheet with scale..... | 141 | 193 | 177 | | | 186 |
| 8. Open Hearth Steel—Sheet without scale..... | 169 | 175 | 185 | | | 150 |
| 9. Special sheet Steel with scale... | 121 | 460 | 307 | | | 160 |
| 10. Special sheet Steel—without scale..... | 137 | 276 | 254 | | | 149 |
| 11. Bessemer Rail Steel..... | 91 | 95 | 123 | 51 | 59 | 63.5 |
| 12. Gray Cast Iron..... | 113 | 105 | 91.5 | 59 | 54 | 93 |

Corrosion Constant—100 = .00092 g. pr. sq.in. pr. day = .01426 g. dem. pr. day

the winter period. The use of the "corrosion factor" is in accordance with the practice recommended by Friend.¹ In making measurements all of the corrosion losses were reduced to loss per square inch per day, and the ratio of that loss compared with the sample chosen as standard constitutes the corrosion factors. In order that these corrosion factors can be converted into actual loss of weight per day there is given the "corrosion constant" which is .00092 g. per sq. inch per day or .01426 g. per sq. dem.

Table I is of greater practical importance since the "Fume test" represents only a special artificial condition not capable of reproduction.

The influence of the seasons upon corrodibility is marked.

¹ The corrosion of Iron and Steel. J. Newton Friend, p. 276.

TABLE II
Corrosion Factors—Fume Test

| Material | (d) 1st Period 75 Days | (d) 2nd Period 75 Days | (e) Combined Period 150 Days | (d) 139 Day Period Summer | (e) 139 Day Period Summer | (ff) Total Period 300 Days |
|--|------------------------------|------------------------------|---------------------------------------|------------------------------------|------------------------------------|-------------------------------------|
| 1. High Purity Iron— $\frac{1}{2}$ " Bar | 147 | 305 | 211 | 134 | 132 | 189 |
| 2. High Purity Iron— $\frac{1}{4}$ " Bar | 146 | 325 | 207 | 117 | 108 | 183 |
| 3. High Purity Iron Sheet with scale..... | 157 | 305 | 193 | | | 160 |
| 4. High Purity Iron—Sheet without scale..... | 128 | 299 | 200 | | | 216 |
| 5. Swedish Iron $\frac{1}{2}$ " Bar..... | 133 | 244 | 144 | 88.5 | 95 | 122 |
| 6. Open Hearth Steel—Boiler Plate..... | 138 | 251 | 179 | 107 | 124 | 111 |
| 7. Open Hearth Steel—Sheet with scale..... | 116 | 280 | 134 | | | 108 |
| 8. Open Hearth Steel Sheet without scale..... | 163 | 337 | 377 | | | 148 |
| 9. Special sheet Steel—with Scale..... | 185 | 303 | 256 | | | 161 |
| 10. Special Sheet Steel—without Scale..... | 173 | 307 | 340 | | | 135 |
| 11. Bessemer Rail Steel..... | 97 | 140 | 87 | 93.5 | 83 | 63.5 |
| 12. Gray Cast Iron..... | 117 | 150 | 115 | 73.5 | 83 | 67.2 |

Corrosion Constant 100 = .00092 G. pr. Sq. In. per day = .01426 G. sq. decm. per day.

The average of the corrosion factors of the twelve materials for winter is 118, for the spring 169, and for the summer and autumn 60.

It is unfortunate that the tests did not cover a 365 day run—but the figures given in the 300 day column may be taken as representing approximately the behavior of the metals when exposed to a year's atmospheric attack. The average 300 day corrosion factor is 111. The corrosion constant being .01426 g. per sq. decm. per day, the amount of corrosion per year is

$$365 \times 1.11 \times 0.01426 = 5.777 \text{ g. per sq. decm. of surface per year.}$$

Assuming a uniform corrosion without pitting the thickness of iron removed by rust per year would be according to the

above figure, and specific gravity of iron taken as 8, .00722 cm., or .00284 inch.

On this basis a 16 gauge sheet, having a thickness of 1/16" when exposed to atmospheric corrosion on both sides would have a life of 11 years. This is a longer life than would actually be attained on account of pitting and other disturbing factors. It is of course not demonstrated by these tests whether there is an acceleration or retardant action during succeeding years.

As to the relative durability of different grades of materials, no absolute conclusions are possible since the samples chosen may not be truly representative—but on the assumption that they may be we have a range from 63.5 as representing the most resistant to 186 for the least resistant or a variation of over one hundred percent.

That a commercial material, even though it may be of a uniform and constant composition and structure cannot be assigned a definite "corrosion factor" is shown by comparison of Table I with Table II. The more resistant metals under atmospheric corrosion become the less resistant under another kind of corrosive atmosphere. That is, the corrosion conditions are important as affecting the relative durability of a given list of materials. Following this line, then, the "atmospheric" corrosion to which these samples were subjected is not necessarily the same as atmospheric corrosion in other sections of the country, and the data obtained cannot be used therefore without reservation.

ACID CORROSION

After having been exposed to atmospheric and fume corrosion for 150 days the samples were ground down to a smooth bright surface and exposed to the standard sulphuric acid test. There were duplicate samples of each material and the results recorded in Table III are the averages of these two determinations. That there were very small errors in measurement was shown by the close agreement between the losses of each of the two corresponding samples.

By comparison of the last column of Table I giving corrosion factors for atmospheric corrosion with the first column of Table

TABLE III
Acid Corrosion

| | (A) Samples after having been exposed to atmospheric corrosion | (B) Samples after having been exposed to fume corro- sion | B/A |
|----|---|--|------|
| 1 | 100 | 140 | 1.40 |
| 2 | 79 | 142 | 1.80 |
| 3 | 67 | 168 | 2.54 |
| 4 | 80.5 | 136 | 1.69 |
| 5 | 320 | 361 | 1.13 |
| 6 | 1960 | 2210 | 1.13 |
| 7 | 5500 | 9000 | 1.63 |
| 8 | 5150 | 11500 | 2.24 |
| 9 | 6710 | 7050 | 1.05 |
| 10 | 7770 | 4450 | 0.57 |
| 11 | 2100 | 3170 | 1.51 |
| 12 | 3330 | 4080 | 1.23 |

Corrosion Constant - 100 = .0072 g. per sq. inch surface per hour.

III giving the corrosion factors for acid corrosion we had a means of judging something of the significance of the acid test. There is seen to be no direct relationship between the two tests. The four materials showing the highest acid corrosion were the ones showing the highest rate of atmospheric corrosion, but the sample showing the least atmospheric corrosion, the Bessemer rail material, has a high acid corrosion rate. While the high purity samples had the lowest rates of acid corrosion, and were likewise below the average in rate of atmospheric rusting, there is no direct relationship as between the respective samples of this class of materials.

By comparison of the acid corrosion with the fume corrosion tests, column 2 of Table III and column 6 of Table II, there is

seen to be no utility of the acid test since the samples most resistant to acid were among the least resistant to the fumes.

A characteristic of the acid test is its extreme sensitiveness, the most corrodible metal being dissolved 116 times as rapidly as the most resistant. The atmospheric test shows a ratio of only 2.9 as between the most and the least corrosive. Evidently there are factors which influence the rate of acid attack which do not enter into atmospheric corrosion.

An interesting phenomenon is shown in column three of the acid corrosion table in that the attack on the metals which had been subjected to fume corrosion was notably greater, with but one exception, than on those which had been subjected to atmospheric attack. Just why this should be is not evident, but it appears that the fume corrosion has had a deep-seated action penetrating into the metal and making it more susceptible to acid corrosion.

INFLUENCE OF SCALE ON RATE OF RUSTING

In making quantitative corrosion determinations, and a comparison of durability of different classes of material the question arises as to the influence of the black scale which comes on commercial sheet; and whether for sake of comparison it is important that all of this scale be removed before beginning a test. This in turn depends upon whether the oxide scale has a protective or accelerating action. There is no doubt that the protective property of mill scale is dependent upon its physical properties, continuity, etc.

It was the purpose in conducting these tests to make comparison of rusting on samples identical in every particular except as to presence of the mill scale. In the above tables, materials Nos. 3, 4, 7, 8, 9, 10, were subjected to this comparison, the odd numbered materials being tested with the scale while from the even numbered materials the scale was carefully removed by mechanical means before the test.

The results of this comparison are presented in Table IV.

TABLE IV
Influence of Scale on Rate of Rusting

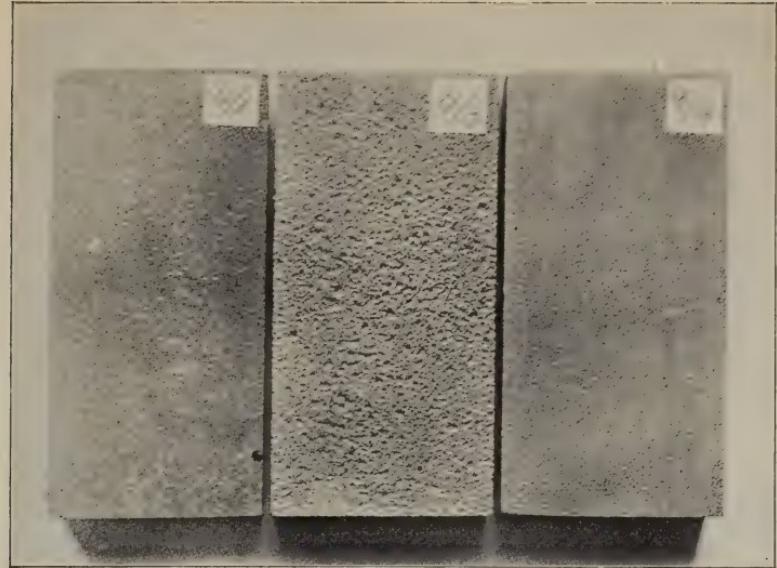
| Material | 75 Day Period | | 150 Day Period | | 300 Day Period | |
|-------------------------------------|---------------|---------|----------------|---------|----------------|---------|
| | With | Without | With | Without | With | Without |
| Atmospheric Test | | | | | | |
| 3 and 4. High Purity Iron..... | 148 | 124 | 149 | 135 | 109 | 90.5 |
| 7 and 8. Open Hearth Mild Steel .. | 141 | 169 | 177 | 185 | 186 | 150 |
| 9 and 10. Open Hearth Special Steel | 121 | 137 | 307 | 254 | 160 | 149 |
| Totals..... | 410 | 430 | 633 | 574 | 455 | 389.5 |
| Fume Test | | | | | | |
| 3 and 4. High Purity Iron..... | 157 | 128 | 193 | 200 | 160 | 216 |
| 7 and 8. Open Hearth Mild Steel .. | 116 | 163 | 134 | 377 | 108 | 148 |
| 9 and 10. Open Hearth Special Steel | 185 | 173 | 256 | 340 | 161 | 135 |
| Totals..... | 458 | 464 | 583 | 917 | 429 | 499 |

Except for the first 75 day period it is shown that the mill scale had an accelerating effect for the atmospheric test and a retardant action for the fume test.

ACCELERATING INFLUENCE OF RUST

It is a generally accepted belief that rust having once formed upon an iron surface this adhering rust exerts an accelerating influence upon the subsequent rate of rust formation: that the adherent rust instead of acting as a protection has a reverse influence.

The tests above recorded present data from which a quantitative idea of the influence of this factor may be derived. Samples marked (a) and (d) in tables I and II were exposed to two successive periods of rusting; the rust having been removed at the end of each period. At the same time similar test pieces (b) and (e) were exposed without disturbance, for the entire

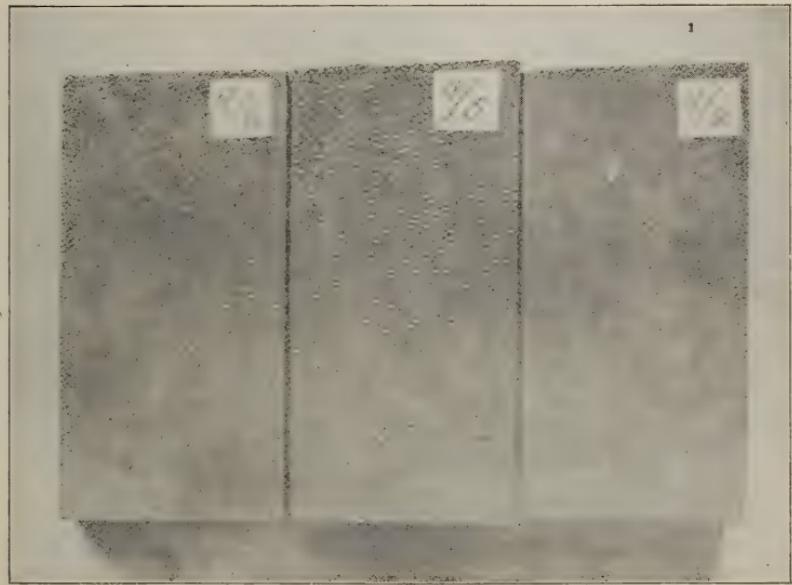


139 Days

300 Days

139 Days

Atmospheric Corrosion—Open Hearth Steel Plate
Fig. 2

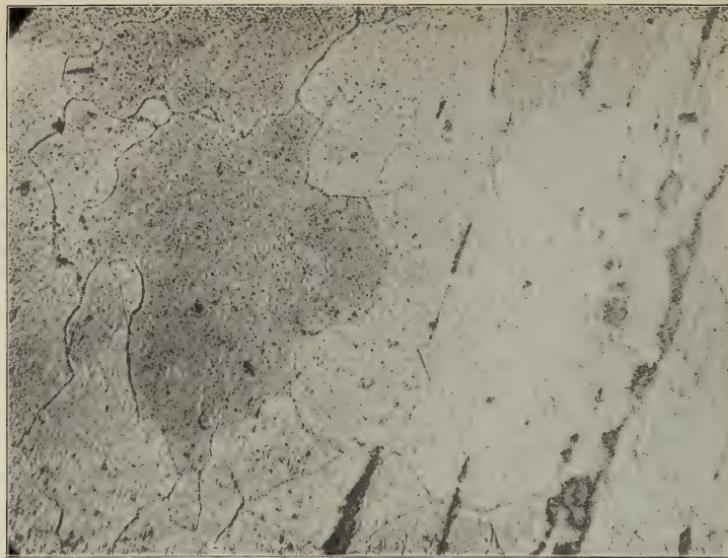


139 Days

300 Days

139 Days

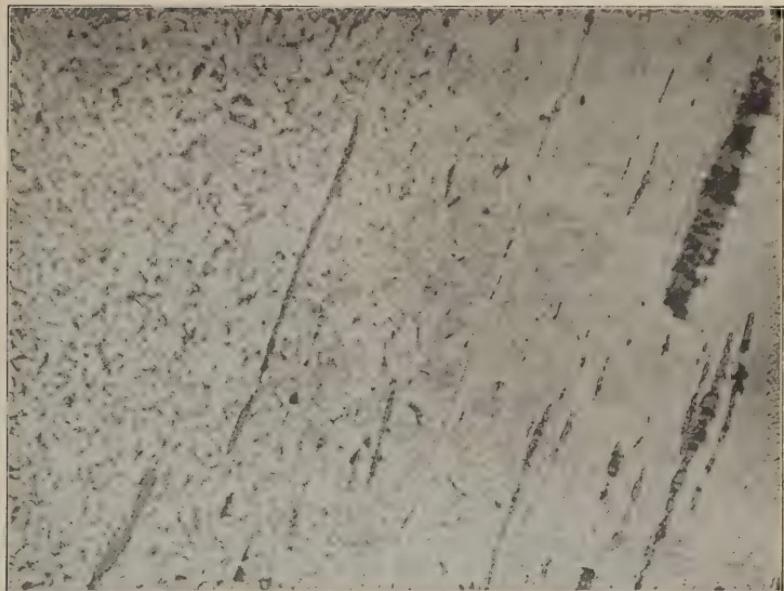
Fume Corrosion—Open Hearth Steel Plate
Fig. 3



X70
Swedish Iron—Low Carbon Areas with Slag
Fig. 4



X70
Swedish Iron—Medium Carbon Area with Slag
Fig. 5



X70

Swedish Iron—Junction of Medium and Low Carbon Areas with Slag Lines
Fig. 6



X70

High Purity Iron—Good Clean Ferrite Structure
Fig. 7



X70

Open Hearth Plate—Ferrite and Small Pearlite Areas Indicating Low Carbon Content. Few Inclusions, Indicating Good Material

Fig. 8



X70

Bessemer Rail Steel—Normal Structure of Rail from Re-heated Billet and Rolled Hot

Fig. 9



X70
Gray Cast Iron—Unetched, Showing Graphite Distribution
Fig. 10



X70
Low Carbon Steel—Special Mechanical Treatment
Fig. 11

TABLE V

Accelerating Influences of Rust on Rusting—Corrosion Factors

| Material | 1st Period 75 Days | 2nd Period 75 Days | Average | Combined Period 150 Days | Accelerating Factor |
|-----------------------|-----------------------|-----------------------|---------|-----------------------------|------------------------|
| Atmospheric Corrosion | | | | | |
| 1 | 100 | 134 | 117 | 154 | 131% |
| 2 | 94.5 | 109 | 101.7 | 143 | 140% |
| 3 | 148 | 135 | 141.5 | 149 | 105% |
| 4 | 124 | 124 | 124 | 135 | 109% |
| 5 | 82.5 | 96 | 89.2 | 141 | 158% |
| 6 | 97 | 123 | 110 | 135 | 122% |
| 7 | 141 | 193 | 167 | 177 | 106% |
| 8 | 169 | 175 | 172 | 185 | 108% |
| 9 | 121 | 460 | 290.5 | 307 | 106% |
| 10 | 137 | 276 | 206.5 | 254 | 123% |
| 11 | 91 | 95 | 93 | 123 | 132% |
| 12 | 113 | 105 | 109 | 91.5 | 84% |
| Fume Corrosion | | | | | |
| 1 | 147 | 305 | 226 | 211 | 93% |
| 2 | 146 | 325 | 235.5 | 207 | 88% |
| 3 | 157 | 305 | 231 | 193 | 83% |
| 4 | 128 | 299 | 213.5 | 200 | 94% |
| 5 | 133 | 244 | 188.5 | 144 | 76% |
| 6 | 138 | 251 | 194.5 | 179 | 92% |
| 7 | 116 | 280 | 198 | 134 | 68% |
| 8 | 163 | 337 | 250 | 377 | 151% |
| 9 | 185 | 303 | 244 | 256 | 105% |
| 10 | 173 | 307 | 240 | 340 | 142% |
| 11 | 97 | 140 | 118.5 | 87 | 74% |
| 12 | 117 | 150 | 133.5 | 115 | 86% |

150 day period. If the presence of rust exerts an accelerating action this will result in the total amount of corrosion from the 150 day samples being greater than for the sum of the corrosion of the two 75 day periods. This relationship is shown in Table V. The first and second columns give the corrosion factors for the two 75 day periods, the third column the average of these two periods. The fourth column gives the corrosion factors for the 150 day period. The ratios of the values of the fourth to the third column give the figures for the last column which indicates whether there has been an accelerating or a retarding influence caused by the presence of rust.

From this table it is seen that when subjected to atmospheric corrosion there has been an accelerating action on all materials

except cast iron; while with the materials exposed to fume corrosion the presence of the rust coating seems to have exerted a protective action on all but three of the materials. It is of course evident that these ratios would be different depending upon the lengths of time of exposure. The accelerating action is probably greater when there is only a small amount of rust on the surface than when the rust increases in thickness.

The deduction of particular interest from this table is that the kinds of conditions by which rusting is produced are of importance, and that external conditions as well as internal structure and purity of material must be considered in studying iron corrosion.

INFLUENCE OF PITTING

It is obvious that the rate of deterioration of iron is measurable not alone by the loss of weight but that the depth of pitting is a factor which must be included. An attempt is made here to give a quantitative idea of this factor. It is unfortunate that all of the samples could not be tested for pitting effect. The thin sheet samples had been rendered too thin to be subjected to accurate grinding for removal of the pit marks and only the bar samples were examined.

The materials Nos. 1, 2, 5, 6, 11 and 12 which had been rusting during the 139 and 300 day periods were filed down and ground smooth until the pit marks had just disappeared and the amount of metal removed by this mechanical operation was determined. This was reduced to weight per square inch and added to the corrosion loss per square inch. This combined value is taken as representing the combined deterioration by rusting and pitting, and the ratio of this amount to that due to rusting alone is indicated by what we choose to call the "Pitting Factor." The results are recorded in Table VI.

The factor of interest drawn from this table is that the combined effect of rusting and pitting under atmospheric conditions is from 3.5 to 6.5 times that as measured by the rusting alone, while under the fume corrosion conditions the pitting is much less pronounced as represented by the corresponding ratios of between limits of 1.68 and 3.96. While the loss by rusting for

TABLE VI
Influence of Pitting—Atmospheric Corrosion

| Description of Material | 139 Day Period | | | 300 Day Period | | |
|--|---------------------------------|--|----------------|---------------------------------|--|----------------|
| | Corrosion Loss g. per sq.in. | Corrosion and Grind- ing Loss g. per sq. in. | Pitting Factor | Corrosion Loss g. persq. in. | Corrosion and Grind- ing Loss per sq. in. | Pitting Factor |
| 1. High Purity Iron $\frac{1}{2}$ " thick | 0.1014 .095 | 0.4874 .456 | 4.8 4.8 | 0.2193 | 1.0433 | 4.76 |
| 2. High Purity Iron $\frac{1}{4}$ " thick | .0752 .0853 | .4072 .4523 | 5.41 5.30 | .230 | 0.885 | 3.86 |
| 5. Swedish Wrt. Iron..... | .093 .0623 | .423 .404 | 4.55 6.52 | .1995 | 0.9105 | 4.57 |
| 6. O. H. Steel Boiler Plate..... | .0658 .0621 | .3398 .3061 | 5.16 4.93 | .272 | 1.022 | 3.76 |
| 11. Bessemer Rail Steel..... | .0764 .0668 | .4344 .3638 | 5.68 5.44 | .1756 | 0.9566 | 5.45 |
| 12. Cast Iron..... | .0763 .0698 | .4223 .3838 | 5.54 5.50 | .253 | 0.888 | 3.51 |

Fume Corrosion

| | | | | | | |
|--|----------------|----------------|--------------|--------|--------|------|
| 1. High Purity Iron $\frac{1}{2}$ " thick | 0.168 .1601 | 0.609 .555 | 3.63 3.47 | 0.5219 | 0.9739 | 1.86 |
| 2. High Purity Iron $\frac{1}{4}$ " thick.... | .1382 .1497 | .4483 .4387 | 3.25 2.94 | .507 | .855 | 1.68 |
| 5. Swedish Wrt. Iron..... | .121 .113 | .3125 .417 | 2.58 3.69 | .336 | .740 | 2.2 |
| 6. O. H. Steel Boiler Plate..... | .1585 .1375 | .5615 .5145 | 3.54 3.74 | .3054 | .7504 | 2.46 |
| 11. Bessemer Rail Steel..... | .1053 .1196 | .4683 .4516 | 4.59 3.78 | .1756 | .555 | 3.18 |
| 12. Cast Iron..... | .0925 .1064 | .3665 .3704 | 3.96 3.48 | .186 | .491 | 2.64 |

the 300 day period is much the greater under the fume conditions the pitting is less marked and the total deterioration is less.

Photographic records of the appearance of each of the samples after corrosion were obtained, a typical one being presented in Figures 2 and 3. This is for the open hearth plate steel. There was a striking similarity of appearance as between the various

materials and it is for this reason that only one is presented here. The fact that there has been less pitting under the fume than under atmospheric conditions is clearly shown.

Microscopic examination was also made of the various samples to determine if possible how the rate of corrosion may have been dependent upon internal structure. Some of these sections magnified to 70 diameters are presented in Figures 4 to 10.

It is a prevalent impression that corrosion, rusting and pitting are dependent upon the impurities in the metal, upon the internal structure, and especially upon segregation; that if there is absolute uniformity, absolute purity, and absence of slag, oxide and other inclusions there will be minimum rusting. These impressions do not appear to be borne out by this investigation. The Swedish iron is shown in Figures 4, 5 and 6, to be markedly heterogeneous there being some areas of pure ferrite, but others of medium carbon content and with slag inclusions. Figure 7 shows a good uniformity in one of the commercially pure irons, while other microphotographs not shown here indicate spots of impurity. In preparing these microphotographs it was the intent to make them representative of the average appearance of the samples rather than to emphasize impurities or non-uniformity.

SUMMARY OF CONCLUSIONS

The range of durability as between various grades of commercial materials when exposed to a 300 day atmospheric test is represented by the ratio of about one to three. When exposed to the acid test the ratio is very much greater, being one to one hundred sixteen.

The average rate of normal atmospheric corrosion under conditions found in Madison, Wis., is 5.777 g. per sq. decm. per year. For a 16 gauge plate exposed on both sides and assuming uniform corrosion this would mean a complete disappearance in about 11 years.

The corrosive action of the atmosphere may be influenced by fumes, and smoke so as to influence in marked degree the durability of iron, and that material most durable under one set of conditions may not necessarily be the most durable under another.

Since the service conditions constitute a vital factor in determining the rust resistant power of iron a study of these conditions is equally important with a study of the materials themselves.

The seasons and the weather conditions have a marked influence on the rate of corrosion.

The sulphuric acid test is not a satisfactory guide for estimating the rust resistant power of a metal. It has a certain usefulness in investigative work but is of little value as a practical test.

The ordinary black scale does not appear to be a retarder of atmospheric rust. Pitting causes deterioration in a year's time approximately three times as great as would rusting if distributed uniformly over the surface.

While impurities in the metal undoubtedly have an influence on the rate of rusting it is evident that while some impurities are detrimental others may be beneficial. Little accurate information appears available on this matter.

Heterogeneity of structure of metal is generally supposed to be antagonistic to durability but this investigation shows that if it is a factor it is one of secondary significance and overshadowed by other factors.

Finally, these results are presented as only tentative since conclusive evidence on a problem so important and complicated as the corrosion of iron and steel can be obtained only by repeated tests upon a large number of samples.

The authors acknowledge indebtedness to E. C. Haag in making many of the measurements recorded in this paper and to the Northern Chemical Engineering Laboratories in the preparation of specimens and coöperating otherwise in the work.

ELECTRICAL PRECIPITATION OF DUST AND FUMES

(COTTRELL PROCESSES¹)
(Demonstration and Exhibit)

LINN BRADLEY

This paper presents a brief review of the processes for precipitating suspended particles from gases by means of high-tension electric currents, and outlines the present applications of the same. A demonstration of some of the principles of the processes will be given after the presentation of the paper, and some features of the past activity and present installations will be described and illustrated by means of a few slides.

Supplementing this discussion of the development of the practical side of the work, a paper will be presented on Thursday afternoon by Dr. Cottrell before the Political Economy and Conservation Section of this Congress, covering the history of the processes. This paper will describe the Research Corporation, which now owns and controls the greater part of the Patent Rights to these processes for the United States.

The Research Corporation is now supervising the installation

¹ Subsequent to the reading of the above paper, Mr. Bradley explained in detail the construction of the small apparatus prepared for demonstrating the Cottrell Processes. The first test was upon the precipitation of cement dust, which was blown through a pipe 6" in diameter. The effect of the high tension current was to collect all of the dust within the pipe. The cement dust was shipped from the plant of the Riverside Portland Cement Co., at Riverside, California, having been collected by the Cottrell Processes at that plant. The dust was placed in a bottle and compressed air introduced in such a manner as to pick up and distribute the dust within it. A test was next made upon some chemical fumes. Compressed air was blown through bottles containing concentrated ammonia and concentrated hydrochloric acid separately, and the chemically laden gases mixed in a chamber just prior to being introduced into the electric treater. Dense fumes of ammonium chloride were thus obtained and the effect of turning on and off the current was demonstrated. A further test was upon tobacco smoke.

of these processes at various plants in its operating territory; all net profits from this development being turned over to the Smithsonian Institution for furthering scientific research. This Corporation is so organized that no profits are obtained by its stockholders or directors. The members of this Congress are referred to the paper by Dr. Cottrell for further details of the Research Corporation, its aims and objects.

In previous articles which have been published in the Journal of Industrial and Engineering Chemistry, Proceedings of The American Institute of Mining Engineers and elsewhere, Dr. Cottrell has explained the original work on these processes and has also described the general operation of several installations, more particularly in the metallurgical fields. The application of the same to the Portland Cement Industry forms the subject of another paper presented on the opening day of the present Congress, by Mr. Walter A. Schmidt, before the Silicate Industries Section.

The problem of removing suspended particles from gases becomes a serious one when the volume of gases is very large, or the temperatures high, or the gases contain materials which exert a corrosive action upon flues, chambers and apparatus.

The variety of problems and conditions is very large, but they may be divided into three general classes, as follows:

First—Where the composition of the gases is such that they are the cause of complaint on the ground of nuisance and damage to property.

Second—Where the values contained in the gases render their recovery quite necessary on the ground of economy, but where the gases do not constitute a nuisance.

Third—Where the gases may be considered sufficient cause for complaint, and yet contain values which should be recovered.

In the first class, and as a further illustration of the growing range of application of these processes, may be mentioned the black smoke, ashes and cinders coming from the stacks of some of the large power plants where the boilers are being forced. In some of these plants the operating departments have endeavored in various ways to purify their gases, so as to avoid any complaints. In a small plant, with proper arrangement

of boilers, arches, settings and flues, the stack gases seldom give rise to complaint. Undoubtedly the proper method of attacking this problem is to endeavor to obtain proper combustion. However, there are a great many instances where complete combustion is not desired, and in such cases these processes may prove to be of value in overcoming the nuisance due to black smoke or other suspended particles. Among its other activities the Research Corporation is at present engaged in demonstrating the removal of such suspended particles by the electrical precipitation processes at one of the largest power plants in the City of New York. In this plant there are nearly one hundred boilers, connected to four smoke stacks, approximately three hundred feet high by twenty-two feet in diameter. The average velocity of the gases through these stacks is estimated at thirty-eight linear feet per second. During the evening, when the peak load is on the station, it is necessary to force the boilers, so that they are delivering perhaps 100 to 150% in excess of their rated capacity. Automatic stokers are used, but even with the greatest care, considerable ashes and cinders are caught up by the draft and carried toward the stacks. The cross flues have been enlarged in order to reduce the velocity of the gases, but although some of the heavier particles are deposited in these chambers, the exit gases carry a fairly large amount of cinders and ashes. Experiments upon this particular material indicate that the greater portion of the large particles can be caught if the velocity in the flue is reduced sufficiently and ample time is allowed for the particles to settle out of the draft by gravity; but flues large enough to produce this result would be prohibitive. Some particles are so light that a slight movement of the gas easily keeps them in suspension. If we endeavor to increase their weight by water sprays or similar means, we interfere with the draft, and may not find our efforts successful, because some particles resist moisture and are extremely difficult to remove by this method. If we are able to construct an apparatus, which will not be prohibitive in size, and does not seriously interfere with the draft, whereby we can overcome the buoyancy of the particle in the gas and remove it from the influence of the draft, we will succeed in cleaning the gas of the suspended particles. The

actual net amount of energy necessary to withdraw these particles from the moving gas is very small indeed. The problem is to design and construct such an apparatus, then to place the electrical charge upon the particle and introduce sufficient energy to compel the particle to migrate to some point away from the rapidly moving gas. This may be accomplished by the use of high-tension direct current, either intermittent or continuous. Discharge electrodes and collecting electrodes are placed in a chamber and the gas containing the particles passed between them. The gas is ionized and some of the ions collect upon the particles, thereby charging them, electrically. Inasmuch as the charged particles are within a strong electric field of constant polarity, they are driven to the collecting electrodes. The construction of these electrodes may be varied considerably, to suit the special conditions of each particular problem. In most instances, the collecting electrodes are grounded. To meet different conditions, various forms of electrodes are used, as will be seen in the lantern slides to follow. The voltages used range from 15,000 up to as high was 50,000 or more, depending upon the size of installation and conditions of the gases to be treated. It will be realized that it is desirable to operate on gases at a high velocity and during a short period of time, in order that the installation may be made as small as possible. Results at present in hand indicate the feasibility of removing the cinders, ashes and black smoke from these power house gases at a reasonably high velocity and without any serious interference with the draft. Samples of the collected material are here upon the desk for your inspection.

Much more might be said about this problem, but it may be more to the point, in this general survey, to mention some phases of the work bearing upon other industries.

Shortly after the organization of the Research Corporation, last February, investigations were undertaken on the gases arising from the smelting of the slimes obtained in electrolytic copper refining. The copper, as received at the electrolytic refinery, generally contain some gold, silver and other precious metals, as well as arsenic, selenium, tellurium and many other elements, in small quantities. During the purification of the copper by

electrolysis, most of these impurities settle out from the electrolyte. This sediment, called electrolytic slimes, is then treated in another department, primarily for the recovery of the gold and silver. It is common practise in some refineries to dry this slime and then give it a furnace treatment. The volatile elements are driven off in the gaseous state and subsequently condensed in the flues. During the furnace treatment, considerable silver is vaporized, some of which condenses quite near the furnace exit. At this point in the flue dust may be found assaying very high in silver. Considerable gold may also be found at this point, probably having been carried over mechanically. Further along the flue, arsenic, antimony, selenium and other elements, or their compounds, condense, thus forming a thick chemical fume. It is interesting to note the tendencies of the various compounds to deposit. For instance, some of the silver compounds or metallic particles are very light and finely divided, and it is extremely difficult to effect a satisfactory recovery by settling chambers, centrifugal dust apparatus or by water sprays and scrubbers. Gold has been found a long distance from the furnaces, but as a rule it is the first to deposit. The influence of one or several volatile metals upon the volatility of other metals, especially at various temperatures, has not been studied very extensively, but most authorities state that the loss of silver is increased in the presence of lead or zinc. Probably arsenic or antimony also exert an influence upon silver. It would be interesting and of considerable value to consult curves of vapor tensions of these various elements under the varying conditions of these refinery gases. Samples of this kind of dust from various refineries show it to have a range of at least from 100 to 2,000 ozs. of silver per ton. The gold content is not apt to vary so greatly. Fume has been collected after passing through water scrubbers (so arranged that the gas was saturated and carried water particles in suspension) and found to still contain large amounts of precious metals. The character of the fume will depend, of course, upon the composition of the copper received at the refinery, as well as upon the operations of the refining furnaces. It is almost impossible to filter this gas, because of its corrosive action upon the filtering medium, and its tendency

to clog the same. Results obtained upon these gases lead to the conclusion that practically all of the values can be readily recovered by the electrical precipitation processes, thereby insuring a greater net profit in these departments. The problem of recovering the values from the dust collected is receiving considerable attention. If all the collected dust is fed back into the furnace, the highly volatile elements will again be driven off, subsequently condensed and, in turn, collected. This will permit the impurities to concentrate and increase to such a point as to be objectionable.

Experiments are now being conducted with a view to facilitating the recovery of the precious metals in a pure state from this precipitated fume. The proposed method may open up an opportunity for improvements in the present practise of treating these electrolytic slimes.

The electrical precipitation processes have been in steady use for the collection of sulphuric acid mist from parting kettles, in one silver refinery for a number of years, and have given excellent results. Another application recently developed is the equipment of acid concentration stills, so as to recover the small amount of sulphuric acid being carried away by the gas. The installation is very compact, the power consumption small, and very little attention is required. For installations of this character special devices for overcoming insulation difficulties and promoting the ionization by the discharge have had to be worked out. The pubescent electrodes are one of the most important features in installations of this type.

One of the large lead smelters in the western portion of the United States is installing the processes on their roaster stack. Godfrey machines and Dwight-Lloyd sintering machines are employed, delivering their gases to a common flue. This flue has a cross section of such size that the average velocity of the gases is about 500 linear feet per minute. A large amount of the very heavy particles are deposited in the first 200 feet of flue, but the fume is being discharged from the stack, after having travelled a much greater distance. Preliminary tests were made on these gases at a point about 150 feet from the stack base. The temperatures varied from 100°C. to 150° C. During these prelimi-

nary tests, the ore charges upon the sintering machines were varied and checked against the assays of the dust recovered electrically, during the day, in order to ascertain how the different charges influenced the loss of lead. Assays of recovered dust varied from 20% to 45% lead during this period. Even at this distance from the roasters, considerable silver and an appreciable amount of gold was found in each sample. The dust recovered was dry and could easily be handled, as it was so dense and compact that a little draft did not blow it away. The smelter is now proceeding with an installation on a larger scale and it is expected that considerable values will be recovered. Furthermore, this installation may make it possible to push the roaster department to a greater tonnage, due to the ability to collect any materials carried in suspension by the gases. In some roasters, a fairly large percentage of sulphur trioxide is produced. Apparatus can easily be designed to handle this character of gas successfully, without undue deterioration.

Another recent application of these processes is in the removal of tar and suspended carbon from illuminating gas. Mr. Walter A. Schmidt has directed the work upon the gas manufactured from crude petroleum at one of the gas plants near San Francisco. A complete clearance of all visible particles was obtained. In the eastern part of the United States the work of Prof. A. H. White, of the University of Michigan, should be mentioned. Under the auspices of the Michigan Gas Association, Prof. White has conducted extensive investigations, primarily upon the removal of tar from gas manufactured from soft coal. The results were so gratifying that negotiations have been instituted for a larger installation, for this purpose. The tar is collected upon the collecting electrodes and runs off into sealed chambers. This field promises to be a very wide one.

Several months ago, prior to the organization of the Research Corporation, Dr. F. G. Cottrell made arrangements with Prof. R. K. Duncan, of the University of Pittsburgh, whereby the latter arranged to use the Cottrell Processes for conducting investigations upon the smoke problem of the City of Pittsburgh. Dr. Strong, Dr. Benner and others have been of assistance in this important problem.

Many other problems of a similar nature to some of those mentioned above have been brought before us and an effort will be made to adopt the processes to them at the earliest possible date. There are many places adjacent to New York City wherein considerable values may be recovered and at the same time, improve the atmosphere, at least in so far as suspended particles and obnoxious fumes are concerned.

Much more of the details of the processes themselves or their application to specific problems might be given, but it would prolong this paper unnecessarily. I sincerely trust that the above general survey may be of value as well as interest to the members of this Congress.

I have constructed a rough apparatus for demonstrating the action of direct current upon dust and fume and will now endeavor to show the operation of these processes upon a small scale.

INFLUENCE OF VARIOUS ELEMENTS ON THE CORRODIBILITY OF IRON

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Incidental to an extensive investigation on electrolytic iron and alloys produced therefrom, as carried out under a grant made a number of years ago by the Carnegie Institution, tests were made upon the corrodibility of a number of alloys. Acknowledgment is made to Mr. B. F. Bennett for his assistance on this particular phase of the work.

The electrolytic iron which has been used as a basis for the alloys, when compared to materials commercially available, may be taken as essentially pure and in making up the alloys care was taken to exclude impurities as far as possible. The method of preparing the test samples consisted, first in melting the electrolytic iron or the electrolytic iron alloy in closed graphite magnesia lined crucibles heated in an electrical resistor furnace. Upon cooling down the small ingots weighing from one to two pounds were forged into rods and strips. Only those alloys which would forge readily into shape were included in these tests.

From the forged bars, samples were taken for chemical analysis and through the courtesy of Messrs. Booth, Garrett and Blair, of Philadelphia, the determinations given in the first column of the attached table were obtained.

The corrosion test samples were cut to a size of about 2" x 1" x $\frac{1}{8}$ " thick. (5 cm. x 2.5 cm. x 3.1 mm. thick.) They were exposed to the weather conditions in Madison, Wisconsin, for a period of 162 days, from July 1909 to February 1910. Before exposure, all samples were ground to a uniformly smooth surface. After the removal of rust by the ammonium citrate method, all samples were subjected to an accelerating acid corrosion test, using a twenty per cent sulphuric acid, and immersing for a period of one hour. Each sample was suspended by itself in a beaker to avoid errors by presence of other materials.

Some results of interest were derived from these tests, though how far they may be of practical value as indicating the influence of various elements on commercial material is problematical. The materials used are practically carbon free as well as having such minor quantities of sulphur, phosphorus, silicon and manganese, (except where intentionally added) as to have in all probability little effect. There is widely prevailing belief that the effect of any element added to iron is to increase corrodibility by furnishing galvanic couples. A great majority of these test samples indicate the reverse; that is, a greater durability for the alloys than for the electrolytic iron base.

Comparisons between the corrodibility of electrolytic iron and certain forms of pure commercial iron on the market indicate that electrolytic iron is more corrodible both in the atmosphere and in acids. In fact no quantitative comparisons have been attempted as between the alloys produced in this investigation and commercial materials. As an approximate indication, however, ranges are given for tests on commercial materials at the bottom of the table for the experimental alloys.

ELECTROLYTIC IRON

The electrolytic iron for which data is given in the table is not introduced as a sample of the purest that can be made but rather the average material, but as a good representative standard for comparison. As a matter of fact, during the course of the tests, as will be noted at the foot of the table of data, figures were obtained upon various grades of iron and steel of commercial grade and of widely varying degrees of purity; and in these results may be noted values of corrosion both higher and lower than those of the electrolytic iron sample.

So far as this particular sample is concerned it shows nothing especially striking in resistance to corrosion either in acid or in the atmosphere.

In the acid test in particular it does not fall in line with the commonly accepted view that a close approach to purity would indicate a high resistance to acid attack. On the contrary this particular material has been attacked even more severely than most of the alloy samples tested at the same time.

ALUMINUM.

In this series there is not enough data to warrant conclusive deductions. So far as the sample with .067 per cent of aluminum is concerned this may be taken as corresponding to iron free from alloying agents. The second sample carrying 1.33 per cent of aluminum, shows an even higher attack by acid than the one of the lower aluminum, but there has been a slight falling off in the atmospheric corrosion. However, there has been nothing striking in either case.

ARSENIC

In view of the fact that the presence of small amounts of arsenic in sulphuric acid pickling solutions decreases markedly the rate of the attack, it has been suggested frequently that arsenic present as an alloying constituent of steels might make such steel more resistant to corrosion, particularly to acid corrosion. This, however, appears to be an erroneous assumption as increased corrosion in acid has been noted by Heyn and Bauer and by Berthier. No satisfactory or conclusive work seems to have been done on the resistance of these materials to atmospheric influences.

Our results cover a series in which the arsenic ranges from .29 per cent to 3.56 per cent and we find a fair resistance to the acid attack, which resistance falls off appreciably with increase of arsenic content. On the other hand the corrosion in the atmosphere is somewhat on a par with that of the electrolytic sample and there would seem to be no particular merits in the use of arsenic alloys for resisting atmospheric corrosion.

From the point of view of physical qualities, also, this series would not be of particular merit, since the brittleness and weakness resulting from the addition of arsenic would be serious. Addition of arsenic seems to result in high magnetic qualities but it is an element which is difficult to add, and if of service from the corrosion point of view it would have to be added in very large amounts and there would thus result a structurally or mechanically poor material.

COBALT

In view of the close relationship in the general properties of cobalt and nickel, it might be natural to expect that the use of these elements as alloying agents would result in somewhat similar properties. The series here tested, however, in which the cobalt varies from 1.3 to 1.5 per cent does not point to any close relationship. The resistance to acid of this series is not particularly striking but does fall off appreciably with increasing cobalt content. The same general effect is noted in the atmospheric tests; but while the corrosion is fairly low, there is not the same resistance to atmospheric attack as is obtained by the addition of the same quantity of nickel. This series shows a fairly close relationship in the rates of atmospheric and acid attack.

To use cobalt for the purpose of making a material highly resistant to corrosion would seem to demand considerable quantities of this element. There would be no advantage, therefore, in the use of this metal as compared with nickel, in view of the high relative cost of the cobalt.

COPPER

The influence of copper upon the corrosion of iron and steel, and to some extent as well, upon the other physical properties is, at the present time, a matter of controversy. So far as the resistance to acid attack is concerned, particularly to sulphuric acid, the evidence seems to be convincing that copper additions result in marked decrease in the rate of such attack. There is a tendency also, not supported by conclusive tests, to believe that copper additions will likewise increase the resistance to atmospheric corrosion.

The series herein tabulated, in which the copper ranges from 0.089 per cent to 7.05 per cent have the expected high resistance to acid attack and also show a low corrosion in the atmosphere. The latter is of particular interest, inasmuch as the values are consistently low throughout the series and the markedly beneficial results seem to be obtained from even small amounts of added copper.

In view of the materially improved physical properties result-

ing from one to two per cent of copper additions, together with the low cost of such addition and the corrosion resistance herein noted, it would seem that this series is of particular promise and worthy of extended study. The quality, both mechanically and from the corrosion point of view, is entirely comparable with that resulting from the use of corresponding amounts of nickel and, of course, there is a materially lessened cost for the addition.

The exact reason for the decreased corrosion is somewhat a matter of speculation. Considering that iron and copper form solid solutions, at least up to three per cent or thereabouts of copper addition, or well within the limits of commercial utility, we should expect the structure of resultant alloy to be one of perfect homogeneity. There should, therefore, be no internal influence tending to promote increased electrolytic action and the effect of the dissolved copper should at the very worst be only neutral as far as corrosion is concerned. In fact, increased resistance to corrosion might be expected, since the solid solution of the two elements might decrease the solution tendency of the iron; or if the iron finally goes into solution it may leave a deposit of copper forming a film and protect the underlying metal from further attack. The presence of such a copper film has been observed repeatedly in the course of etching of samples for microscopic examination and has been noted by other investigators during acid attack of copper-iron-alloys. This speculation seems to be confirmed by the tests herein enumerated.

LEAD

But one alloy of this series was tested and that contained only 0.061 per cent of this element. The acid corrosion is the same as that observed by the electrolytic iron while the atmospheric corrosion has dropped to about half the figure of electrolytic iron. Not enough data is at hand, however, to warrant any deductions regarding the influence of lead upon the corrosion of iron.

MANGANESE

The supposedly increased corrosion of modern steels as compared with the older iron has generally been ascribed to the pres-

ence of manganese which is present in the later day materials as a result of modern process of manufacture. It may be, however, that the manganese is blamed for results due to other elements associated with it, or perhaps to other factors resulting from modern conditions of manufacture.

So far as our tests show in this series, which runs from 0.50 per cent manganese to 10.42 per cent manganese, there is nothing worthy of particular comment either in the acid or atmospheric corrosion. There is considerable inconsistency in the results and the atmospheric tests in particular seem to indicate a slight increase of corrosion with increase of manganese content, though in all cases the corrosion was less than for the electrolytic iron alone.

The alloying relations in this series are those of solid solution, in this respect similar to the copper-iron-alloys in the useful range. We have, therefore, a homogeneous structure and no internal causes for electrolytic action. However, in view of the very similar properties of the two metals there would probably result but little change in the solution tendency of the alloy as compared with the iron itself. Also there would be no deposition of a protective film as was mentioned in the copper series, since manganese is attacked very much like iron and would rust away in a similar manner. Consequently rust once formed from solution of either metal should aid, rather than retard further progression of the corrosion.

NICKEL.

This series shows alloys notably good both in the acid and atmospheric tests. There is a general tendency for increased resistance with increased nickel content.

In the region of nickel content such as is used in practice, about three per cent, we note a marked falling off in the atmospheric corrosion. The hindrance to the general use of this property is the relatively high cost of the nickel addition and it would seem that these alloys would not offer particular merit unless the use of the material is also warranted by the increased strength resulting from the addition. The highest resistance noted lies well up in

the series; that is, at ten per cent nickel and above. Such alloys would be beyond the range of general commercial utility, not only because of the high cost of the nickel but because of the hardness and brittleness and generally disadvantageous physical properties in this region of the series.

The alloying relations of the nickel and iron are those of solid solution and it would seem that the protective effect is due perhaps to the same reasons cited in the case of the copper-iron-alloys; that is, we would have very probably a markedly decreased solution tendency and in case of any corrosion, it would result in a solution of the iron and the consequent concentration of the nickel as a surface protecting film.

SELENIUM

There was tested but one alloy in this series with the very low content of 0.017 per cent of selenium, consequently no particular deductions can be drawn. The acid resistance in this particular sample is very low while the corrosion in the atmosphere is noticeably high.

SILICON

In this series the silicon content varied from 0.23 per cent to 2.82 per cent. The corrosion values are in general high and somewhat conflicting. In fact, this series seems to have suffered the greatest corrosion noted. There has been a general tendency for increase in the atmospheric corrosion with increase of silicon content but not a very material increase.

There seems to be an inclination to assume increased resistance to corrosion in the silicon steels, but the only reliable data appears to be that obtained upon acid tests and mainly upon acid tests of the alloys of high silicon content. Here a compound of iron and silicon becomes the principal constituent and the resistance to acid is probably due largely to this.

So far as ordinary amounts of silicon are concerned its use seems to be disadvantageous both in acid and atmospheric corrosion. Also, silicon behaves much like arsenic and while it results in good magnetic qualities, the resultant steels are otherwise poor physically, being brittle, weak and hard to work.

SILVER

Although alloys were made in which the added amount of silver was as high as ten per cent, the resultant alloys actually indicated a maximum of 0.69 per cent retained, and the series here cited has a silver content varying from 0.28 per cent to 0.69 per cent. There is no particular merit in this addition so far as either acid or atmospheric corrosion is concerned and all of the figures are closely comparable to that obtained with electrolytic iron alone. There is of course no particular commercial significance attached to the use of iron-silver-alloys because of the relatively high cost of the addition.

TIN

This series has a tin content varying from 0.28 to 1.56 per cent. In the lower end of the series the resistance to acid attack is particularly good but the corrosion in acid increases perceptibly with the higher content of tin. As far as the atmospheric tests are concerned there is nothing of particular moment. There is a slight falling off however with increase of tin.

The iron-tin-alloys are somewhat similar in their general properties to the iron-arsenic and iron-silicon alloys—that is, all of these additions result in improved magnetic quality of material but at the expense of the physical, and the resulting alloys are brittle and weak and hard to work.

TUNGSTEN

The tungsten varied from 0.40 per cent to 23.86 per cent. In the acid test the results are all good, some of them very strikingly so; but there is a general irregularity in the figures. The same is true in regard to the atmospheric tests with a seeming tendency towards decreased corrosion with increased tungsten content.

However, the general results are not especially worthy of attention and considering the fact that any markedly decreased corrosion is obtained only after high tungsten additions, these alloys do not offer special value from the corrosion standpoint, since with the high tungsten additions we are entering the tool steel range of alloys of high cost and extreme hardness and brittleness.

CONCLUSIONS

These tests covering several series of alloys of iron with other elements do not seem to point to any quantitative relations as between the acid and atmospheric corrosion.

So far as the atmospheric tests are concerned, numerous alloys can be noted in which the corrosion is less than in the electrolytic iron. The copper series would seem to offer particular advantages in view of the beneficial results obtained with small copper additions and because of the consistently low values throughout the series. Again these benefits are obtainable without prohibitive cost for the addition agent.

| | Acid Corrosion | | Atmospheric Corrosion | |
|-----------------------|----------------|--------------------|------------------------------|----------------------------------|
| | | g. per sq. dem. | Lbs. per sq. ft. per year | Kg. per sq. meter per year |
| Electrolytic iron.... | | 1.300 | 0.1025 | 0.499 |
| Aluminum..... | 0.067% | 0.628 | 0.110 | 0.513 |
| | 1.333 | 0.760 | 0.080 | 0.390 |
| Arsenic..... | 0.292 | 0.448 | 0.0830 | 0.405 |
| | 0.430 | 0.815 | 0.0703 | 0.343 |
| | 0.915 | 0.405 | 0.0870 | 0.425 |
| | 1.810 | 0.131 | 0.0720 | 0.352 |
| | 3.862 | 0.086 | 0.0640 | 0.312 |
| | 4.141 | 0.102 | 0.0740 | 0.361 |
| | 3.562 | 0.144 | 0.0630 | 0.306 |
| Cobalt..... | 1.035 | 0.705 | 0.049 | 0.239 |
| | 2.000 | 1.020 | 0.070 | 0.342 |
| | 4.055 | 0.356 | 0.042 | 0.205 |
| | 5.052 | 0.257 | 0.042 | 0.205 |
| Copper..... | 0.089 | 0.178 | 0.052 | 0.254 |
| | 0.202 | 0.095 | 0.039 | 0.190 |
| | 0.422 | 0.059 | 0.055 | 0.268 |
| | 0.592 | 0.112 | 0.050 | 0.234 |
| | 0.804 | 0.104 | 0.053 | 0.259 |
| | 1.006 | 0.067 | 0.046 | 0.225 |
| | 1.510 | 0.147 | 0.046 | 0.225 |
| | 2.005 | 0.091 | 0.051 | 0.249 |
| | 3.990 | 0.093 | 0.035 | 0.171 |
| | 5.070 | 0.087 | 0.031 | 0.151 |
| | 6.160 | 0.143 | 0.041 | 0.200 |
| Lead..... | 7.050 | 0.186 | 0.033 | 0.161 |
| | 0.061 | 1.300 | 0.056 | 0.273 |
| Manganese..... | 0.505 | 0.560 | 0.055 | 0.268 |
| | 1.000 | 0.520 | 0.080 | 0.390 |
| | 2.000 | 0.725 | 0.062 | 0.302 |
| | 3.000 | 1.110 | 0.067 | 0.327 |
| | 10.419 | 0.352 | 0.089 | 0.435 |

| | Acid Corrosion | | Atmospheric Corrosion | |
|---------------|----------------|--------------------|------------------------------|----------------------------------|
| | | g. per sq. dem. | Lbs. per sq. ft. per year | Kg. per sq. meter per year |
| Nickel..... | 0.270 | 0.6330 | 0.059 | 0.288 |
| | 0.560 | 0.5470 | 0.071 | 0.347 |
| | 1.070 | 0.5070 | 0.058 | 0.283 |
| | 1.930 | 0.1920 | 0.023 | 0.112 |
| | 7.050 | 0.2260 | 0.038 | 0.185 |
| | 8.170 | 0.1250 | 0.029 | 0.141 |
| | 10.200 | 0.0910 | 0.027 | 0.132 |
| | 11.290 | 0.1230 | 0.027 | 0.132 |
| | 12.070 | 0.0840 | 0.024 | 0.117 |
| | 13.010 | 0.2370 | 0.031 | 0.151 |
| | 19.210 | 0.0720 | 0.018 | 0.088 |
| | 22.110 | 0.0254 | 0.020 | 0.098 |
| | 25.200 | 0.0540 | 0.023 | 0.112 |
| | 26.400 | 0.5540 | 0.021 | 0.102 |
| | 28.420 | 0.1550 | 0.021 | 0.102 |
| | 35.090 | 0.1830 | 0.018 | 0.088 |
| | 47.080 | 0.1600 | 0.0126 | 0.062 |
| | 75.060 | 0.0490 | 0.0044 | 0.0215 |
| Selenium..... | 0.017 | 0.190 | 0.1385 | 0.676 |
| Silicon..... | 0.233 | 1.630 | 0.104 | 0.509 |
| | 0.603 | 1.190 | 0.076 | 0.370 |
| | 1.033 | 0.850 | 0.106 | 0.518 |
| | 1.897 | 0.800 | 0.124 | 0.606 |
| | 2.826 | 1.270 | 0.130 | 0.635 |
| Silver..... | 0.281 | 1.020 | 0.065 | 0.317 |
| | 0.492 | 1.760 | 0.090 | 0.430 |
| | 0.581 | 1.340 | 0.073 | 0.356 |
| | 0.691 | 1.170 | 0.092 | 0.450 |
| Tin..... | 0.288 | 0.284 | 0.069 | 0.337 |
| | 0.342 | 0.350 | 0.039 | 0.190 |
| | 0.686 | 0.386 | 0.049 | 0.239 |
| | 1.568 | 1.030 | 0.058 | 0.283 |

| | Acid Corrosion | | Atmospheric Corrosion | |
|---------------|----------------|-------------------|------------------------------|----------------------------------|
| | | g. per sq. dm. | Lbs. per sq. ft. per year | Kg. per sq. meter per year |
| Tungsten..... | 0.406 | 0.363 | 0.076 | 0.371 |
| | 0.925 | 0.088 | 0.062 | 0.302 |
| | 2.334 | 0.086 | 0.062 | 0.302 |
| | 3.553 | 0.332 | 0.063 | 0.308 |
| | 5.982 | 0.304 | 0.060 | 0.293 |
| | 9.849 | 0.398 | 0.040 | 0.195 |
| | 13.641 | 0.365 | 0.049 | 0.239 |
| | 23.866 | 0.183 | 0.044 | 0.215 |

Various grades of low carbon iron and steel..... 0.300 to 0.73

High Carbon Steel..... 0.278

Cast Iron—Scale removed..... 0.770

AN ELECTROLYTIC METHOD FOR THE PREVENTION OF THE CORROSION OF IRON AND STEEL

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INTRODUCTION

According to the electrolytic theory of corrosion, when iron is oxidized in the wet way, it first goes into solution as ferrous ions. The ferrous ions are then oxidized, by the oxygen present in the water, to ferric ions, and precipitated as ferric hydroxide. Simultaneous with the formations of ferrous ions, hydrogen is liberated on the surface of the iron. The passage of the iron from the atomic to the ionic state and of the hydrogen from the ionic to the atomic state is accompanied by a transfer of electricity. The ferrous ions derive from the metal surface a charge of positive electricity, the hydrogen ions give up a charge of positive electricity and a current flows through the metal from the point where hydrogen is liberated to the point where iron is dissolved.

If iron and a metal having a greater "solution tension" than iron, for example zinc, be immersed in acid solution and connected externally through a wire, zinc will go into solution, hydrogen ions will be liberated on the iron and current will flow through the wire from iron to zinc. The potential difference between zinc and iron is opposed to the potential difference between iron and electrolyte and neutralizes the force required to pull the positively charged iron ions away from the negatively charged surface of the iron electrode. Consequently iron does not go into solution.

In place of zinc, other conducting materials, e.g. carbon, may be used as the anode and the EMF required may be furnished from an external source. In this way electric energy derived from either a battery or a generator may be used to protect metals from corrosion under water.

A vast amount of work, both theoretical as well as experi-

mental, has been directed to the study of the causes of corrosion and the development of methods for its prevention, and the literature on the subject is extensive.¹

Very little attention, however, seems to have been given to the development of an electrolytic method for the prevention of corrosion. An electrolytic method has been used to some extent, for the protection of boilers.²

This method consists in submerging a bar of zinc in the boiler water and connecting the zinc electrically with the boiler plates. After the experiments described in this paper were begun it was found that an electrolytic process for the protection of metals had been patented by an Australian inventor.³ The writers have been unable to find any data published by the inventor.

In a paper presented before the Sydney, Australia, Section of the Society of Chemical Industry, G. Harker,⁴ describes experiments on the prevention of the corrosion of iron by electrolysis. He determined the current density necessary to prevent the corrosion of steel plates submerged in N/25 H₂SO₄, tap water, sea water and "dilute acid." The results of Harker's experiments, which furnish the only data on the subject which the writers have been able to find, will be discussed in connection with the results of our own experiments.

EXPERIMENTS BY F. M. STANTON

Experiments to devise an electrical method for the prevention of the corrosion of steel immersed in acid water were undertaken at the Pittsburgh Experiment Station of the Bureau of Mines in May 1911, by Mr. F. M. Stanton, with the co-operation of Dr. J. C. W. Frazer.

¹ See Cushman and Gardner "Corrosion and Preservation of Iron and Steel," New York; McGraw-Hill.

"List of References to Books and Magazine Articles on Metal Corrosion and Protection." Bulletin, Carnegie Library of Pittsburgh, July, 1909.

² J. H. Paul, "Corrosion in steam boilers." Trans. Soc. Engineers, V. 31, Page 147.

³ See Western Electrician, Vol. 58, Page 326, 1911.

⁴ G. Harker and J. McNamara, "Electrolysis as a means of preventing the corrosion of iron and steel." Journ. Soc. Chem. Ind., Vol. 29, Page 1286, 1911.

Stanton's experiments included laboratory experiments and tests on plates immersed in the Monongahela river. In the laboratory experiments, steel plates 6 m.m. x 19 m.m. x 51 m.m. were suspended in N/5 H₂SO₄, in separate vessels. In one vessel a carbon rod was suspended near the steel plate, and connected to the positive pole of a storage battery, the negative pole of which was connected with the steel plate. The steel plate in the second vessel was not protected. After 24 hours exposure it was found that the unprotected plate had lost in weight 1.8100 grams and the protected plate only 0.0012 grams.

In the tests with plates submerged in the Monongahela river a much smaller current density was used than in the laboratory experiment and the protection against corrosion was much less complete. The plates used in these tests had the following dimensions: 6"x8"x $\frac{1}{8}$ ". The protecting current was furnished by a 2 volt accumulator. The loss in weight of the two plates at the end of fifteen days immersion was for the protected plate 0.7 grams and for the unprotected plate 10.9 grams.

EXPERIMENTS TO DETERMINE CURRENT DENSITY REQUIRED TO PREVENT CORROSION

Mr. Stanton left the service of the Bureau in July, 1911, and the work was interrupted until December, 1911, when experiments were resumed by the present authors and Mr. A. E. Hall.

The object of the experiments to be described was to determine the current density required to prevent the corrosion of steel plates in acid water, under various conditions.

EXPERIMENTS IN APPARATUS TYPE I

The first method of determining the protective effect of small currents was to suspend an iron plate of the dimensions shown in Figure 1, in an 800 cc. flask parallel to a $\frac{1}{4}$ " carbon rod and $\frac{1}{2}$ " from it. Using storage batteries as a source of EMF, a current was passed from the carbon rod through dilute sulphuric acid to the iron plate. The current regulation was accomplished by the use of variable resistances and the current measured by the

drop in potential over a known resistance, by means of a Siemens and Halske millivolt meter; electrical connections were always completed before any acid was introduced into the flask and the current regulated immediately thereafter. In order to save time six such flasks were used in each experiment.

The results of the first series of experiments are shown graphically in figures 2 and 3. The experiments represented by the curves in Figure 3 were made under uniform conditions, except that the duration of the test was varied. These experiments indicated that a certain definite current density must be maintained in order to reduce the corrosion loss to a minimum. On account of the poor agreement between the results of individual experiments, a second type of apparatus was designed.

EXPERIMENTS WITH APPARATUS TYPE II

In order to eliminate as far as possible any error due to differences in acid concentrations about the iron plates, all the test plates were immersed in a common vessel. Another improvement was the employment of an acid reservoir, and a constant level device by means of which fresh acid could be fed into the containing vessel, at any desired speed, and the excess electrolyte syphoned off through the level bottle into the overflow. The vessel was a porcelain lined cylindrical dish of about 2250 ccs. capacity and the plates were supported by a thin wooden cover at points on a circle 4" in diameter and at whose center the carbon rod anode was suspended. The plates were set equidistant from each other and of course from the anode.

Six experiments were conducted according to this scheme and the acidity of the electrolyte was determined at the end of each run. There was always a considerable falling off in acid strength which could be eliminated to a large degree by increasing the rate of acid feed. For example, at the end of a 27 hour run, starting with N/10 H_2SO_4 , the acidity was 85/1000 normal. As all the plates, however, were subjected to the same variation in the corrosive element the loss in weight of the plates should be comparable.

The curves in Figure 4 represent the plate losses for experi-

ments 11 and 12 in which Apparatus Type II was used. While the results do not check exactly, they are more consistent than those of the previous experiments. The indications from the experiments of series I and II are that a current of 0.4 milli amps. per square inch (figuring $\frac{1}{3}$ of the back of the plate as is customary) will prevent 93 to 94% of the corrosion action of H/10 H₂SO₄ in still water.

EXPERIMENTS WITH APPARATUS TYPE III

The apparatus finally adopted, Type III, is shown in Figure 5. It differs from Type II chiefly in having a greater capacity—4½ liters—and in being provided with an attachment for stirring the electrolyte. The plates were arranged as before, except that they were set 2½" from the carbon rod instead of 2" in order to keep them under water when the electrolyte was rotating rapidly. For stirring a low power, hot air engine gave fairly constant speed and could be run over night. In order to be able to calculate our current densities with greater accuracy, all surfaces of the plates except the one facing the anode were protected by painting with Bakelite Lacquer. An application of four or five coats have a good smooth surface impenetrable to acids.

The first few experiments using the final apparatus were run with the stirrer rotating at 660 R. P. M. and, under these conditions, currents, that had protected the iron plates almost completely in still water, were absolutely useless. On cutting down the stirring rate to 35 R. P. M. in N/100 acid small currents were again effective and runs could be checked with a fair degree of accuracy.

Figure 6 shows the results of experiments using N/100 H₂SO₄ as electrolyte and with the stirrer running at 35 to 40 revolutions per minute. In this series of experiments the electrodes were removed from the electrolyte and their loss in weight determined, at frequent intervals. The curves in Figure 6 show that the plates having a current density of .4 milli-amperes per square inch or less, continued to lose weight during the entire period of the experiments. Plates protected by current densities greater than 0.4 milli-amperes per square inch exhibited a marked initial

corrosion and thereafter no further loss in weight. The initial loss in weight of the plates protected by current densities greater than 0.4 milli-amperes is probably due to the fact that at the start of the experiment the plates were covered by a film of air, and that the oxygen of the air film acted as a depolarizer. Some time elapsed, therefore, before the plates became completely polarized and during this period they were only partially protected by the current. The difference between the rate of loss in weight of the unprotected plate during the initial period and the rate during the remainder of the experiment is probably due to a difference in the structure of the original surface of the metal and that of the interior portion, as well as to the action of the film of air surrounding it at the beginning of the experiment.

EFFECT OF PASSING OXYGEN THROUGH ELECTROLYTE

On account of the depolarizing effect of oxygen it was to be expected that the amount of oxygen present in the electrolyte would be an important factor in determining the speed of corrosion. Figure 7 shows the results of a series of four experiments made to ascertain the effect of increasing the amount of oxygen in the electrolyte. The composition of the electrolyte and the speed of the stirrer were the same in all four experiments, viz., N/100 H₂SO₄ and 35 R. P. M. The lower curves represent two experiments with the usual amount of oxygen present. The electrolyte was prepared by adding sulphuric acid to distilled water without any special precautions either to exclude the air or to aerate the solution. In experiments 38 and 39 represented by the two upper curves, the electrolyte was saturated with oxygen by rapidly bubbling oxygen through the electrolyte during the experiment. The curves show that increasing the amount of oxygen in the solution accelerates the speed of corrosion very materially, the loss of weight in 24 hours being about twice as great when oxygen was passed through the electrolyte, as when oxygen is supplied by diffusion only. It follows from this that the rate of corrosion in any acid solution will depend on the amount of aeration to which the solution is subjected.

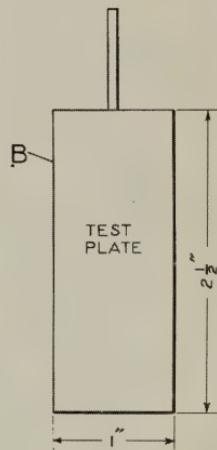
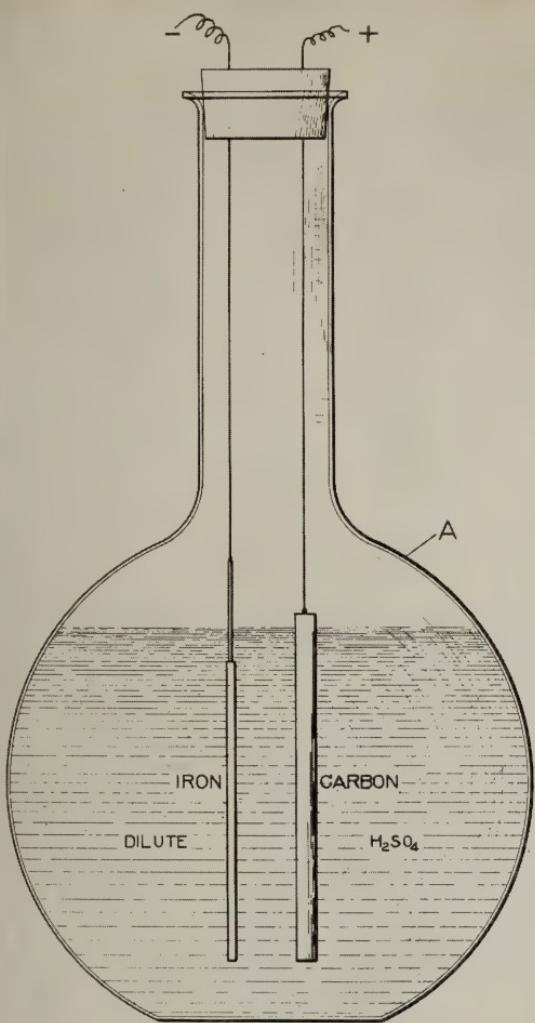


Fig 1. APPARATUS TYPE I

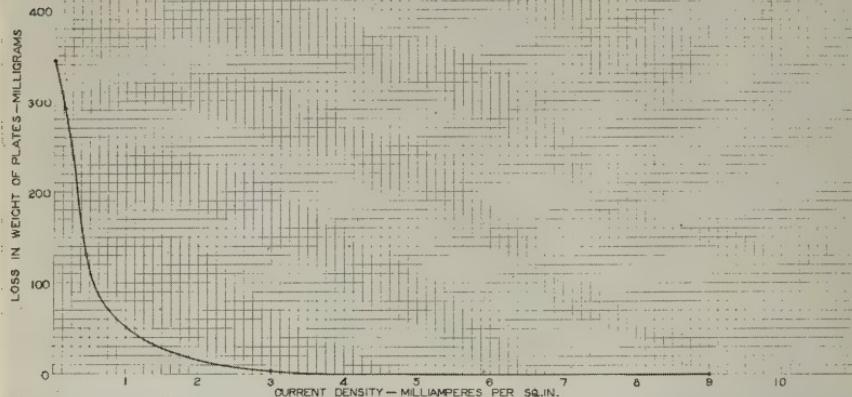


Fig. 2. RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY
APPARATUS TYPE I., DURATION OF TEST 45 HRS. $\frac{N}{5} \text{H}_2\text{SO}_4$ ELECTROLYTE UNSTIRRED

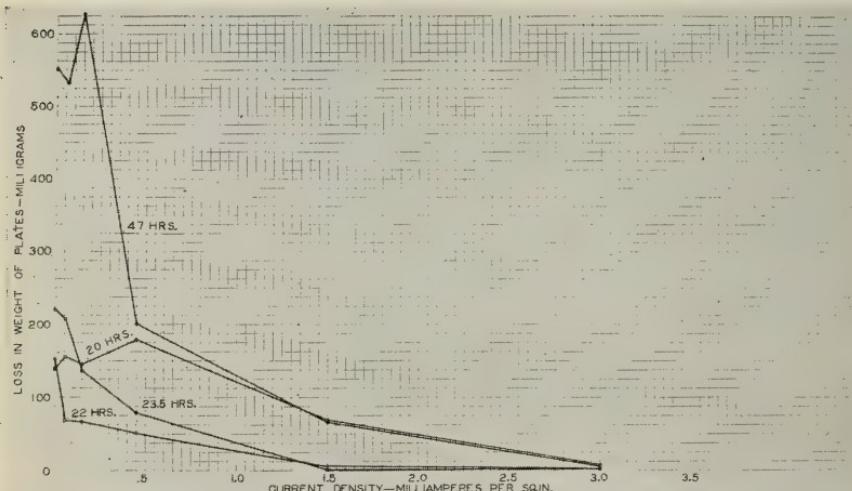


Fig. 3. RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY
APPARATUS TYPE I. $\frac{N}{10} \text{H}_2\text{SO}_4$ ELECTROLYTE UNSTIRRED

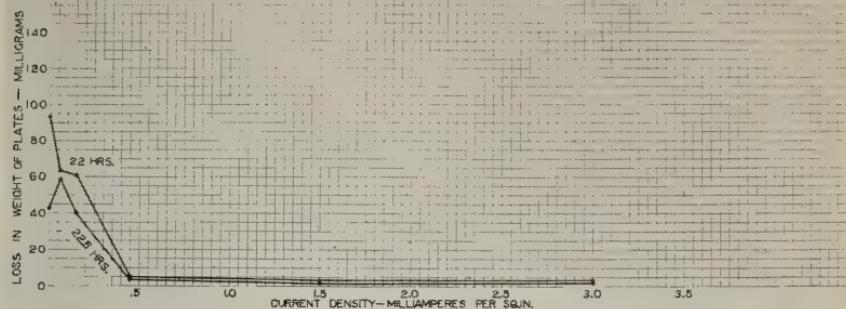


Fig. 4. RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY
APPARATUS TYPE II $\frac{1}{10}$ M_g SO₄ ELECTROLYTE, UNSTIRRED

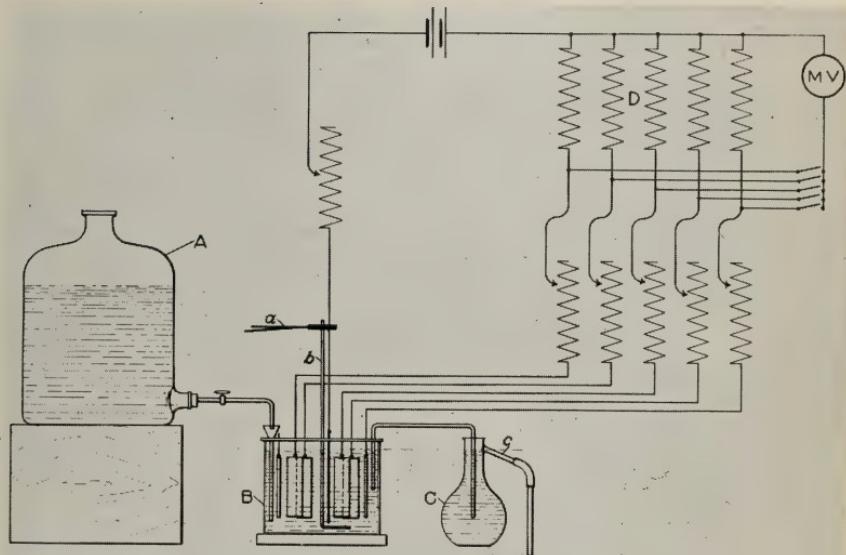


Fig. 5. APPARATUS TYPE III

A, acid reservoir; B, electrolytic tank; C, level bottle; D, known resistance; a, belt to motor; b, stirrer; c, to overflow

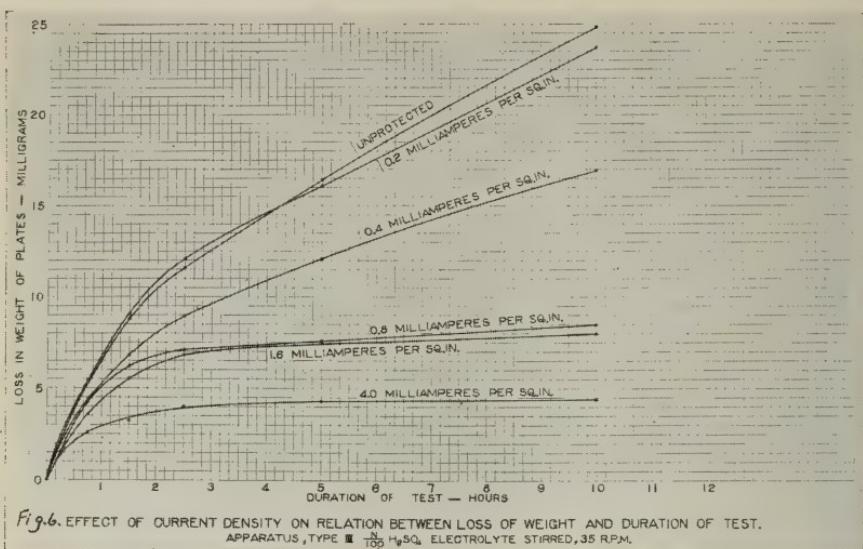


Fig. 6. EFFECT OF CURRENT DENSITY ON RELATION BETWEEN LOSS OF WEIGHT AND DURATION OF TEST.
APPARATUS, TYPE II, $\frac{N}{100}$ H_2SO_4 ELECTROLYTE, STIRRED, 35 R.P.M.

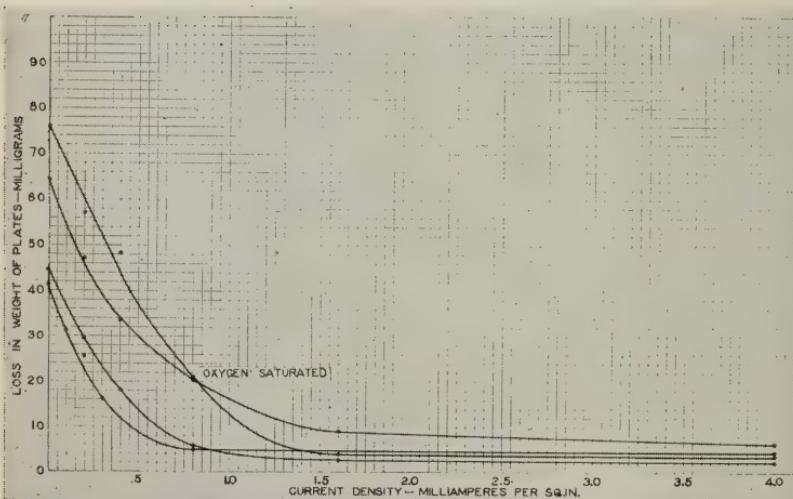
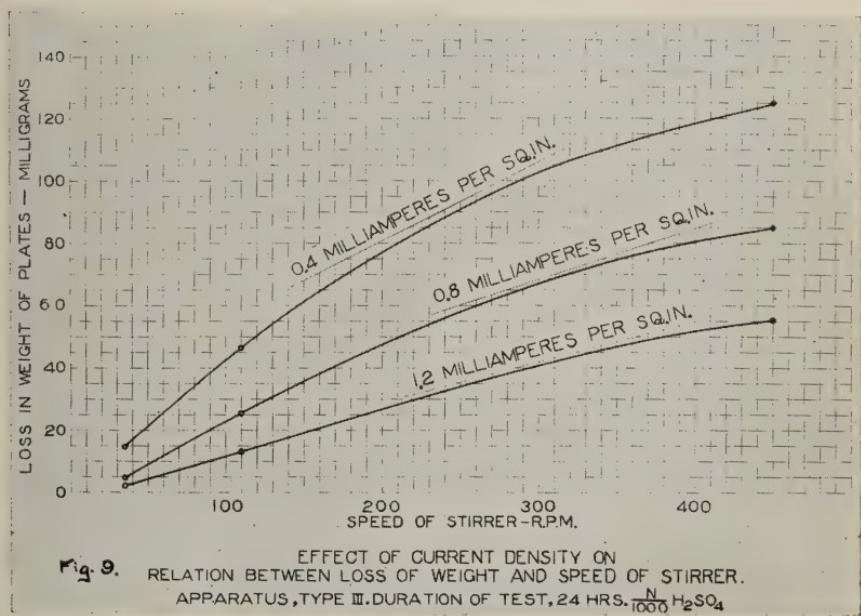
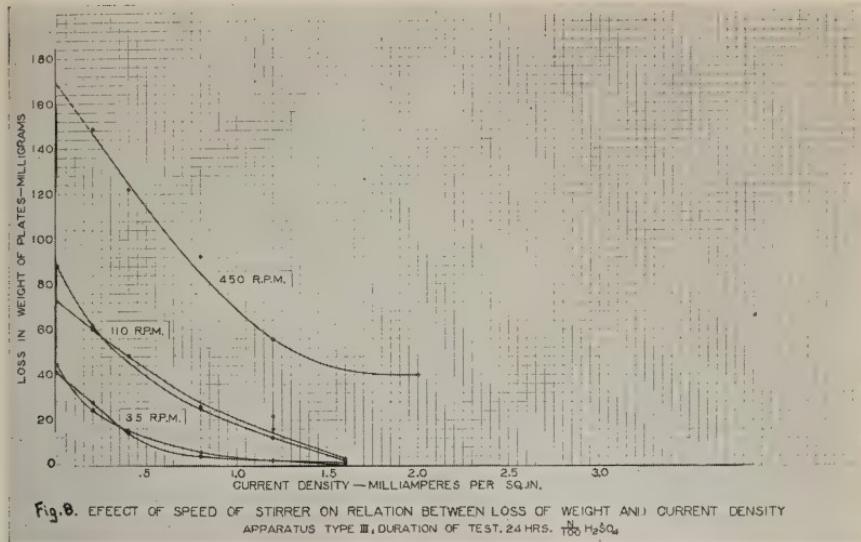


Fig. 7. EFFECT OF OXYGEN ON RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY
APPARATUS TYPE II, DURATION OF TEST, 24 HR., $\frac{N}{100}$ H_2SO_4 ELECTROLYTE, STIRRED 35 RPM.



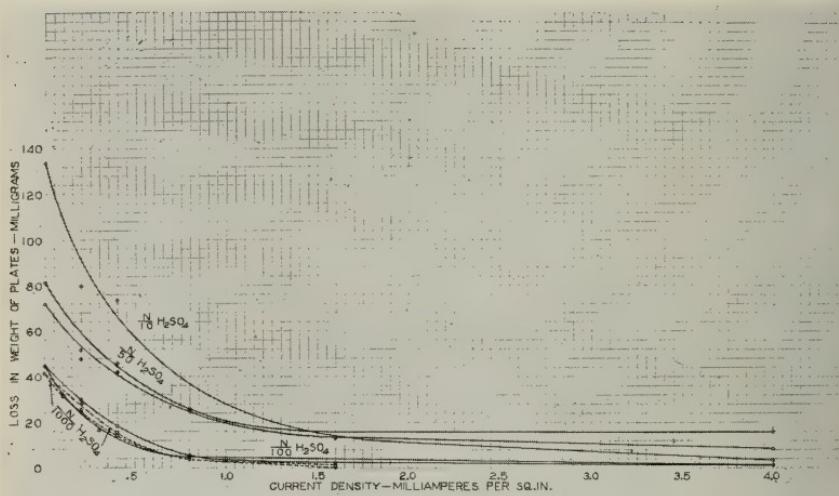


Fig. 1a. EFFECT OF ACID CONCENTRATION UPON RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY.
APPARATUS TYPE III. DURATION OF TEST, 24 HRS. ELECTROLYTE STIRRED 36 RPM.

EFFECT OF STIRRING

The enormous acceleration of corrosion produced by extremely rapid stirring, 660 R. P. M. has been noted on page 495. On account of the magnitude of this effect, a series of experiments was made in which the speed of the stirrer was the only variable. The results are shown in Figure 8. An examination of the curves shows that, the other conditions being constant, the loss in weight by corrosion varies directly as the rate of stirring. The increase in the speed of corrosion with the increase in the rate of stirring is further illustrated by Figure 9, in which the loss in weight of the plates, for several different current densities is plotted against the number of revolutions of the stirrer per minute.

These results demonstrate that the rate of flow of acid solution over the metal surface is an important factor in determining the amount of corrosion and the current density necessary to protect the metal. The very considerable increase in the speed of corrosion produced by circulation of the electrolyte is not surprising since the flow of solution over the metal surface not only hinders the exhaustion of hydrogen ions in the vicinity of the anode, but provides a continual supply of oxygen and tends to destroy any film of hydrogen which may form on the surface of the cathode.

ACID CONCENTRATION

That the rate of corrosion of iron or steel in sulphuric acid solutions increases with the acid concentration is well known. While the acid concentration in the natural waters in which the corrosion of iron ordinarily occurs is much below 1/100 normal,—the concentration used in most of the experiments described,—the application of the method to move concentrated solutions seemed of sufficient interest to justify experiments with stronger solutions. Accordingly a series of experiments was made in which the concentration of sulphuric acid was varied from 1/1000 normal to 1/10 normal. The results are represented by the curves in Figure 10. They indicate that, although a considerably greater current density would be required, the method would be effectual even in N/10 H₂SO₄. The curves for experiments with 1/100

normal and 1/1000 normal acid are practically identical, showing that between these limits of acid concentration there is no change in the rate or corrosion greater than the limit of error of observation. This result though unexpected, was confirmed by repeated experiments.

POTENTIAL OF IRON ELECTRODES

In the majority of the experiments, in addition to measuring the current flowing into the different electrodes, the potential of the individual electrodes was measured against a zinc electrode. Potential readings were made with a Siemens & Halske millivolt meter of 450 ohms resistance in series with a resistance of 17550 ohms. The results are given in table I. The agreement between the potentials of electrodes having the same current

TABLE I
ELECTRODE POTENTIALS
E.M.F. (Protected—Unprotected Plates)

| Current | Current density milli amperes per sq. inch | Exp. 30 | Exp. 31 | Exp. 32 | Exp. 35 | Exp. 36 | Exp. 37 | Exp. 38 | Exp. 39 | Exp. 40 |
|---------|--|---------|---------|---------|---------|------------|------------|---------|---------|---------|
| 0.50 | 0.2 | 0.021 | .004 | -.021 | -.024 | .004 | .012 | .027 | -.005 | -.004 |
| 1.00 | 0.4 | | -.003 | -.012 | .003 | .022 | .008 | -.018 | -.051 | -.024 |
| 2.00 | 0.8 | 0.198 | 0.025 | .102 | .078 | .073 | .044 | .012 | .000 | .015 |
| 4.00 | 1.6 | 0.433 | 0.114 | .237 | .186 | .187 | .108 | .102 | .081 | .090 |
| 10.0 | 4.0 | 0.723 | 0.289 | .429 | .372 | .392 | .304 | .315 | .295 | .303 |

Rate of stirring = 35 R. P. M.
Acid = N/100 H₂SO₄

density is only fair. In N/100 H₂SO₄, and with a rate of stirring of 35 R. P. M., a current density of 0.8 milli amperes per square inch generally produced an increase in the potential of the iron electrode of about 0.04 volts. (In the table potential differences are positive when the potential of the protected plate is positive to the unprotected plate, i.e. when the potential difference between

the zinc electrode and the protected plate is decreased by the protecting current). As small an increase in the potential of the best plates as 0.04 volts sufficed, therefore, to protect them against corrosion. This effect is too small,—especially in view of the variations found between the results of different experiments made under like conditions of acid concentration and rate of stirring,—to be of value as a measure of the degree of protection against corrosion offered by the current.

CURRENT DENSITY

In the experiments which have been described, the following factors were found to influence the current density required to protect the corrosion of steel plates submerged in sulphuric acid solutions.

- (a) Rate of stirring of electrolyte.
- (b) Amount of oxygen present.
- (c) Acid concentration.

Of these the last named is probably of least importance especially in dilute solutions.

The rate of stirring of the electrolyte is by far the most important factor. In practice the supply of oxygen in the immediate vicinity of submerged metal surfaces depends, largely, on the rate of flow of solution over the metal surface.

With the lowest rate of stirring used in the experiments, 35 R. P. M., and in acid concentrations not greater than 1/1000 normal, a current density of from 0.5 to 0.8 milli amperes reduces the corrosion loss to a negligible quantity. While with the stirrer rotating at a speed of 450 R. P. M. and a current density of 2.0 milli amperes the corrosion loss amounted to 25 per cent of the loss on the unprotected plate.

HARKER'S EXPERIMENTS

From his experiments referred to above, P.—Harker concluded that in employing the electrolytic process the current required to prevent corrosion might be calculated from the rate of corrosion of iron or steel under the given condition and the

electro chemical equivalent of iron. This he confirmed by one set of experiments in which, however, iron anodes were used. In experiments with a platinum anode, Harker found that the protection afforded by the current to the iron cathode was somewhat less than when an iron anode was used. He concludes "that the electrolytic process does not actually prevent metal from entering the solution from the cathode for where the rate remains constant, deposition is taking place from the anode, yet the tendency of the metal to pass into solution is much diminished."

APPLICATION OF HARKER'S RULE

In all of the experiments made by the present authors, a carbon anode was used. Harker's method of calculating the current density required to prevent corrosion was based on experiments with an iron anode. If, then, as Harker suggests, the protective action of the current is largely due to the transfer of iron from the anode to the cathode it would not be expected that his method would hold for experiments with a carbon anode.

The method offers, however, such a simple procedure for arriving at the proper current density required to prevent corrosion that it seemed worth while to apply it to the results of the authors' experiments. In table II are given the results of the authors' experiments to which have been added the values for the current densities calculated from the loss in weight of the unprotected plates and the electro chemical equivalent of iron. The "observed" values for the current densities in column 6 were obtained graphically from the curves in Figures 2, 3, 4, 7, 8 and 10. The agreement between the observed and calculated values is remarkably good. The differences are well within the experimental error.

It may, therefore, be concluded that Harker's method of calculating the current density required to prevent corrosion, from the loss in weight of the metal under the given conditions, is not limited to cases in which an anode of the same metal is used.

TABLE II

| Fig. | Exp. | Acid conc. | Stirrer R.P.M. | Length of run hours | Observed current density Milli-amp. per square inch | Calc. current density milli amps. per square inch. | Losses Milligrams Unprotected plate | |
|------|------|------------------------|----------------|---------------------|---|--|-------------------------------------|---------------------|
| 2 | 4 | N/5 | — | 45. | 3.0 | 2.2 | 344.6 | Apparatus Type I. |
| 3 | 6 | N/10 | — | 47. | 3.0 | 3.4 | 551.5 | |
| 3 | 7 | " | — | 20. | 3.0 | 2.0 | 140.5 | |
| 3 | 9 | " | — | 23.5 | 1.5 | 2.7 | 221.0 | |
| 3 | 8 | " | — | 22. | 1.5 | 2.0 | 151.5 | |
| 4 | 11 | " | — | 22.5 | 0.45 | 0.5 | 43.0 | Apparatus Type II. |
| 4 | 12 | " | — | 22. | 0.45 | 1.2 | 93.5 | |
| 7 | 39 | N/100 Oxygen Saturated | 35 | 24. | 1.6 | 1.3 | 75.9 | |
| 7 | 38 | " | " | " | 1.6 | 1.0 | 64.3 | Apparatus Type III. |
| 7 | 40 | N/100 | " | " | 0.8 | 0.7 | 44.6 | |
| 7 | 30 | " | " | " | 0.8 | 0.7 | 41.4 | |
| 8 | 48 | N/1000 | 450 | " | 2.0 | 2.7 | 170. | |
| 8 | 45 | " | 110 | " | 1.6 | 1.4 | 88.3 | |
| 8 | 46 | " | 110 | " | 1.6 | 1.2 | 72.8 | |
| 8 | 42 | " | 35 | " | 0.8 | 0.7 | 44.5 | |
| 8 | 41 | " | 35 | " | 0.8 | 0.6 | 41.0 | |
| 10 | 51 | N/10 | 35 | " | 1.6 | 2.2 | 133.8 | |
| 10 | 49 | N/50 | 35 | " | 1.2 | 1.1 | 71.3 | |
| 10 | 50 | N/50 | 35 | " | 1.2 | 1.3 | 80.9 | |

THE NATURE OF THE ACTION OF THE ELECTRIC CURRENT

Harker's view that the current does not actually prevent metal from entering the solution from the cathode, and that its protective action is due to the deposition of metal from the anode, is contradicted by the authors' experiments in which carbon anodes only were used. The action of the current is, then, to prevent the formation of ferrous ions at the cathode by increasing its negative charge. In the absence of any depolarizer, especially of dissolved oxygen, an infinitesimal current should produce an electro motive force large enough to neutralize the solution tension of the metal. When oxygen is present, it combines with the hydrogen ions liberated at the cathode and hinders polarization. The supply of hydrogen ions furnished by the current must be equivalent to the supply of oxygen in the vicinity of the cathode before the solution tension of the cathode can be completely neutralized.

CONCLUSION

It has been shown that the corrosion of iron submerged in sulphuric acid solutions may be prevented by imposing a counter E. M. F. The density of the current required to prevent corrosion depends on various factors: acid concentration, amount of dissolved oxygen and degree of circulation of electrolyte. The influence of these factors has been studied and curves have been given showing the current density necessary under various conditions. It has been found that the current density required can be calculated, within the limit of experimental error, from the loss in weight of the metal under the given conditions when not protected.

APPLICATIONS OF DUCTILE TUNGSTEN

COLIN G. FINK, PH.D.

Harrison, N. J.

Less than ten years ago Tungsten was universally conceded to be a very brittle metal. Since the introduction of ductile tungsten,¹ however, large quantities of drawn wire, flexible and strong, are being daily produced for the manufacture of incandescent lamps.

We have studied the physical and chemical properties of this new Tungsten, and have obtained a number of very interesting results. The ductile metal is practically insoluble in all the common acids² and alkalis, its melting point is higher than that of any other metal,³ its tensile strength exceeds that of iron and nickel, its elasticity is twice that of steel, it can be drawn down to smaller sizes than any other metal, and its specific gravity is 70% higher than that of lead.

It was natural that a metal with *such striking properties* as these should soon find applications other than that for incandescent lamps.

ELECTRICAL CONTACTS

Wrought tungsten has been substituted with success for platinum and platinum-iridium as contract points in spark coils, voltage regulators, telegraph relays, etc.⁴ The service far exceeds that for platinum-iridium due to the greater hardness, higher heat conductivity and lower vapor pressure of Tungsten as compared with platinum.

¹C. G. Fink: Trans. Am. Electrochem. Soc. *17*, 229. W. D. Coolidge: Trans. Am. Inst. Elec. Eng. *29*, 961.

²W. E. Ruder: Jour. Am. Chem. Soc. 1912; 387.

³I. Langmuir: Trans. Am. Electrochem. Soc. *20*, 237.

⁴W. D. Coolidge: Trans. Am. Inst. Elec. Eng. *31*, 870.

TUNGSTEN FURNACES

These furnaces are of two types. The type recently described by Winne and Dantsizen¹ consists of an alundum tube wound with tungsten (or molybdenum) wire. To prevent oxidation, the tube is encased in an air tight box with an inlet and outlet for hydrogen. This furnace is admirably well suited for laboratory experiments. Temperatures of 1600°—1800°C. can be easily maintained for hours, whereas platinum at these temperatures would rapidly disintegrate.

A second type of tungsten furnace² is constructed on lines similar to those of the Arsem Vacuum furnace. A Tungsten metal tube takes the place of the helical carbon resistor. The tube is surrounded by a screen and the whole enclosed in an air tight compartment almost identical to that used by Arsem. The compartment is either evacuated or a small quantity of gas, such as hydrogen, is introduced. This furnace lends itself admirably for the study of reactions at very high temperatures, such as the production of artificial gems.

TUNGSTEN GAUZE

We have used this gauze successfully for separating solids from acid liquors. We performed these experiments on a laboratory scale. However, this gauze could well be used on a commercial scale. For example: for the removal of sludge from copper refining baths, and for centrifugal apparatus whenever acid liquids or acid gases are dealt with.

Furthermore, it might be used in apparatus such as described by Cottrell³ for the removal of sulphuric mist from gases. The Cottrell Electrodes consist of three concentric cylindrical screens of iron wire, the inner and outer ones acting as discharge electrodes, whilst the intermediate screen and the outer leaded glass containing vessel act as collecting electrodes from which the deposited acid drains into a leaden pan below.

¹ Trans. Am. Electrochem. Soc. 20, 287.

² U. S. Pat. 1,006,620.

³ Jour. Ind. Eng. Chem. 3, 542.

Tungsten gauze is not attacked by sulphuric acid and would consequently give a much longer life than iron gauze.

WROUGHT TUNGSTEN TARGETS FOR ROENTGEN TUBES

This application has proved to be one of the most interesting. Tungsten is very well suited for targets or anticathodes and the realm of application and efficiency of the Roentgen Tube have been thereby greatly increased.

As has been shown by Coolidge, the high specific gravity, high melting point, high heat conductivity and low vapor pressure make tungsten a far more efficient target than any other metal.

THERMO COUPLES

We are investigating the thermo electric properties of the couple, tungsten molybdenum. The Elector-Motive force increases with the temperature up to about 540° ($12\frac{1}{2}$ millivolts) then decreases and passes through zero millivolt at about 1300° .

We have found this couple very convenient for high temperature measurements in the tungsten-hydrogen furnace.

STANDARD WEIGHTS

A material suitable for standard weights must be hard yet plastic, it must not be easily scratched nor marred, but still not be so hard that it will chip or break; furthermore, it must withstand the action of the atmosphere and finally it must be small in bulk. Now, wrought tungsten can be made so hard that it will readily scratch glass and still be ductile; furthermore the density is high (19.3 to 21.4) and it is unaffected by the atmosphere. Tungsten weights remain wonderfully constant.

TUNGSTEN CELLS

We have taken up the study of the electrochemical behavior of tungsten and have made up a series of cells and combinations. All measurements were made at 25° and compared with the calomel electrode as standard. Our readings for the cell tungsten, aqueous sodium hydrate, KCl, calomel, mercury are:

5 normal NaOH 0.68 volt; 2 N., .62 volt; N, 0.57 volt; $\frac{1}{2}$ N, 0.525 volt; $\frac{1}{10}$ N, 0.50 volt; $\frac{1}{20}$ N, 0.48; $\frac{1}{40}$ N, 0.455; $\frac{1}{80}$ N, 0.445; $\frac{1}{160}$ N, 0.380; and 0.0 N, 0.06 volt. In the last cell the tungsten rod was immersed in distilled water.

The addition of small amounts of impurities to the tungsten metal causes the tungsten sodium hydrate electrode to assume E.M.F. values that approach that of zinc in zinc sulphate. The E. M. F. of the cell Hg-Hg₂ W₃O₁₁ + Na₂WO₄ solid—Na₂WO₄ sat. soln.—solid Na₂WO₄—W was found to be 0.505 and promises to be a good standard cell.

MISCELLANEOUS APPLICATIONS

Besides the applications of tungsten cited many others have been partly worked out and others merely suggested. Owing to its chemical stability the finest sizes of wire down to 0.0002 inches or 0.005 mm. in diameter, are well adapted for galvanometer suspensions and for cross hairs in telescopes. It has also been suggested to use these fine wires in surgical operations in place of the coarser gold and silver wires. A further suggestion is the use of the wire in musical instruments. The tensile strength and elasticity of tungsten wire exceed that of steel. It could be used to advantage in climates where steel is readily corroded.

We are investigating the formation of hydrocyanic acid gas when passing over heated tungsten wire mixtures of nitrogen and acetylene or methane.¹

The heat of formation of HCN is: C₂H₂+N₂=2 HCN - 9400 cal.²

We are making acid proof dishes and tubes out of tungsten, furthermore, tungsten wire recommends itself as a unit resistance since it can be made absolutely pure, can be easily duplicated and is not corroded.

Since tungsten is practically non-magnetic and very elastic it is being tried out in electrical meters, replacing the phosphor-bronze springs. Similarly watch springs could be made. Finally

¹ Compare Lipinski: Zeit. Elektrochemie 17, 287.

² Wartenburg, Zeit. Anorg. Chem. 52, 299.

we might mention; tungsten pen points, tungsten projectiles, tungsten drawing dies, tungsten bearings and jewels, tungsten-knife blades, tungsten electrodes, tungsten wire reinforced asbestos curtains and fire proof coverings, etc.

TABLE OF PHYSICAL AND CHEMICAL PROPERTIES OF DUCTILE TUNGSTEN

Density 19.3 to 20.2.

Tensile strength 322 to 427 Kg per Sq. mm.

Youngs Modulus of Elasticity 42,200 kilograms per Sq. mm. (Steel 20,000).

Melting point 3177 (Langmuir) 3100 + 60 (v. Pirani & Meyer)
Boiling point 3700° (?)

Thermal Conductivity 0.35 grams cal. per cm per sec. per 1° (Pt. 0.166) (calculated see foot note⁴).

Expansion Coefficient 4.3×10^{-6} (Pt. 8.8×10^{-6}).

Specific Heat 0.0358 (Weiss).

Resistivity (25°) hard: 6.2 microhms per cu. cm. annealed: 5.0 microhms per 6u. Cm.

Temperature Coefficient of Resistance 0.0051 ($0^\circ - 170^\circ$).

Magnetic Susceptibility; +.33 (Honda). i.e. practically non-magnetic.

Hardness 4.5 to 8.0 (Mohs Scale).

Insoluble in HCl, H₂SO₄, HNO₃, HF, NaOH, KOH, (aq.) K₂Cr₂O₇ + H₂SO₄.

Soluble in mixtures of HF and HNO₃, and in fused nitrates and peroxides.

The boiling point of the metal has not yet been determined.

The Youngs Modulus of Elasticity we determined with a wire 0.00648 CM in diameter and 784.86 CM long. We found an average value of 42,200 Kilograms per sq. mm. as compared with 20,000 for steel.

The smallest weight (P) was 225 & the largest 1125 grams.

The elastic elongation was 0.35 CM for the smallest weight and 1.65 CM for the largest. The hardness values were determined with the Schleroscope & the values translated into the Mohs scale.

SOME PHYSICAL AND CHEMICAL DATA ON DRY CELLS AND DRY CELL MATERIAL

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In the discussion of a paper on "Dry Batteries" presented recently before the Faraday Society, it was stated as noteworthy that the best of American cells are inferior to the best British types. Without going into the justice of this assertion, perhaps a presentation of some of the characteristics of typical American dry cells may be appropriate at this time. In presenting this paper the writers are indebted to the courtesy of the Northern Chemical Engineering Laboratories and the French Battery & Carbon Company, of Madison, Wisconsin, for permission to publish the following data obtained through a comparative study of various typical American cells.

A somewhat standard method of construction appears to prevail in this country. The anode is a cylinder of sheet zinc which serves also as the container. The electrolyte is a solution of zinc chloride and ammonium chloride held in a layer of absorbent material, usually paper, lying next to the zinc, and separating it completely from the cathode. The cathode consists of a carbon pencil surrounded by a granulated mixture of manganese dioxide, carbon and ammonium chloride. Graphite is also a common ingredient. This granulated mixture is saturated with electrolyte having ammonium chloride and zinc chloride in solution.

TESTING OF BATTERY MATERIALS

The chemical inspection of dry cell materials should include a determination of the purity of these materials as regards the absence of quantities of useless inert substances to indicate the percentage of the materials which contribute to the usefulness of the cells. In addition to this, tests should also be made for compara-

tively small quantities of such impurities as exert an actively injurious effect upon the cell.

The physical properties of some of the materials are of quite as great importance as are the chemical ones. One of the most important of these is the conductivity of the crushed carbon and graphite, and that of the mixtures of these materials with manganese dioxide. The conductivity of crushed carbon and graphite depend upon the raw materials used in their manufacture, the conditions of heat treatment used, and the size composition.

Battery carbon may be prepared from petroleum coke, retort carbon, or coke made from soft coal. The graphite which is used may be either a natural product or that manufactured by electric furnace methods. Crushed carbon and graphite may also be prepared from used furnace electrodes, or from worn out electrodes from electrolytic processes.

For the determination of the conductivities of crushed materials and mixtures an apparatus especially devised for the purpose and shown in Fig. 1 was used. The material to be tested is placed into a porcelain tube 2" long and 1" inside diameter. The bottom of the tube is closed during the test by a removable graphite plug, and the tube is filled flush with the material to be tested. The tube is placed in an upright position and another graphite plug inserted at the top upon which a pressure of 15 pounds is exerted, by means of a suitably arranged lever and weight. A current of one ampere is passed, the graphite plugs serving make connection to the column of granular material. The circuit includes an ammeter and a variable external resistance. The drop in voltage between the graphite plugs is measured by a voltmeter of suitable range. If accurately checking readings are desired, great care must be taken in the manner of applying the pressure to the tube full of granular material. This same testing apparatus is also arranged to test the conductivity and breaking strength of carbon pencils.

A number of samples of crushed graphite and carbon as supplied by various manufacturers and made by various processes have been tested for conductivity. For graphite there have been obtained readings varying between 0.071 and 0.411 ohm and for carbon between 0.188 and 0.637 ohm per linear inch of a column

one inch in diameter. The minimum readings in each case represent a very high grade of material, while the maximum ones indicate materials which are practically useless for most battery purposes. Most of the samples of carbon tested have been crushed so as to pass through about a 20 mesh screen while the samples of graphite will usually pass through a 100 mesh screen.

In comparison with carbon and graphite, the other insoluble ingredient of pulverized dry-battery filler, namely, manganese dioxide has a very low conductivity, so that as far as the final conductivity of the whole mixture is concerned, the manganese dioxide may be considered as practically an insulator. It follows, therefore, that the higher the proportion of MnO_2 in the depolarizing mixture, as compared with the conducting ingredients, the higher will be the resistance presuming, of course, that the size composition and quality of materials remains the same. The curves plotted on the accompanying chart indicate in a general way how the conductivities change with variations in the proportions of conductive to non-conductive materials, and with variations of the size composition for the same proportions by weight. Variations in the conductivity, of ten to several hundred per cent can be brought about by varying the size composition of a mixture with no change in the proportion by weight of the several ingredients.

INSPECTION OF VARIOUS TYPES OF CELLS

Four of the typical brands of cells investigated and concerning which data are given in the tables are designated by the letters A, B, C and D.

It will be noted from the tables that there is comparatively little variation in the composition of these several makes of batteries. Perhaps one reason for this is the strong demand of the American market for a low priced cell, compliance with which places narrow limits on the manufacturer in a desire he may have to improve the quality of the battery by using more expensive materials, or a more complicated structure.

Table I shows the weights, dimensions and physical properties for the several types of batteries. The size composition and the

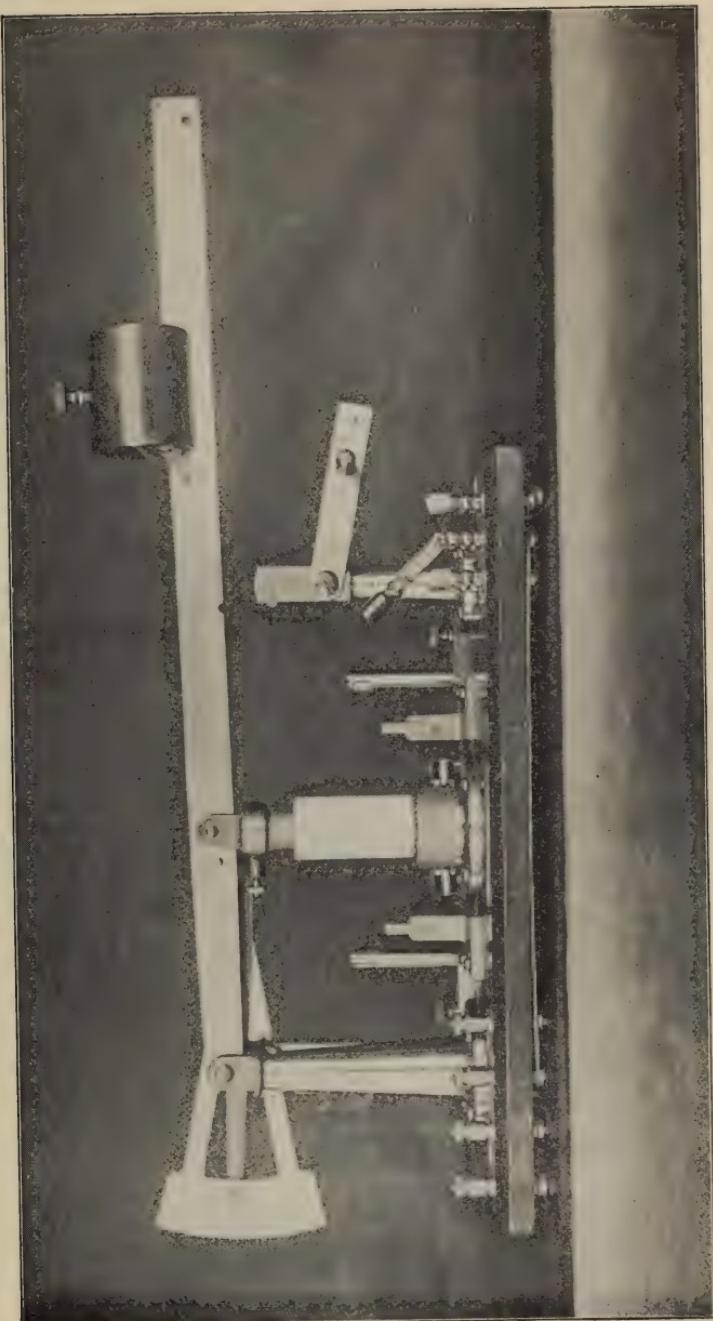
percentage of MnO_2 on the several sizes of the washed and dried mixtures is shown in Table II. In general, it seems that an increase of MnO_2 in the coarser sizes will reduce the internal resistance of the battery. On the other hand there are indications that an increase in the proportion of very finely divided manganese dioxide results in greater depolarizing power per unit weight of the MnO_2 .

Table III shows the quantities of zinc chloride and ammonium chloride present in the solution held in the paper, and in the solution with which the depolarizing mixture is moistened.

The quantity of water present in a No. 6 dry cell varies somewhat for different makes. The upper and lower limits are about 60 and 90 grams. Other things being equal, a better cell probably results from approaching the latter figure rather than from too close an approach of the former.

Measurements of the conductivity of the mixtures were made directly upon the depolarizing material as removed from the batteries, but previous to making the test all of the mixtures were passed through a ten mesh screen. The internal resistance of the battery depends, naturally, not only on the conductivity of the mixture but also the tightness with which it has been compressed in filling the cell. An additional factor influencing the internal resistance that will result from any given mixture, is not only the weight per unit volume of battery space, but also the manner in which the packing is performed.

The remaining common ingredient of dry cells is the least costly of all, but is nevertheless of considerable importance. This is the air occupying the "void" spaces in the depolarizing mixture, that is space not occupied by water, salts, carbon, graphite or manganese dioxide. The volume of voids varies from about 3 to 15 cubic centimeters. All of the data given have reference to a standard "#6" cell, the dimensions of which are $2\frac{1}{2}$ by 6".



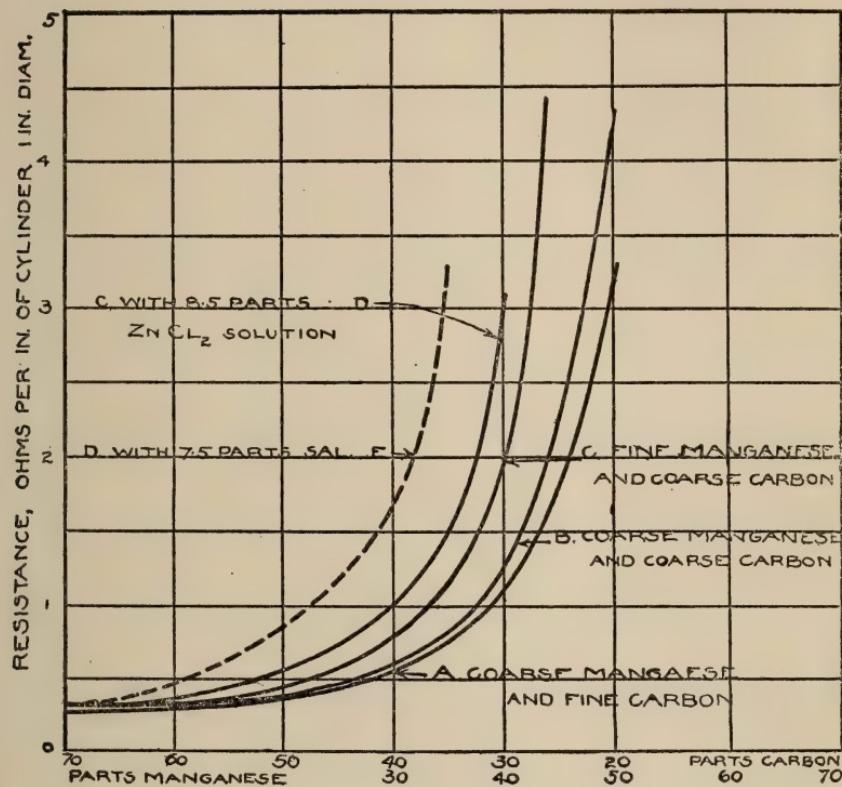


TABLE I

| | A | B | C | D |
|--|------|------|------|------|
| Voltage of cell..... | 1.50 | 1.57 | 1.55 | 1.50 |
| Amperes on short circuit (flash)..... | 33 | 33 | 32 | 30 |
| Weight of cell, grams..... | 980 | 932 | 984 | 942 |
| Weight of moist depolarizing, mixture, grams..... | 642 | 545 | 576 | 574 |
| Weight of Paper lining, wet, grams..... | 61 | 71 | 65 | 72 |
| Diameter of carbon pencil..... | 1" | 1" | 1" | 3/4" |
| Weight of zinc, grams..... | 117 | 110 | 132 | 151 |
| Resistance in ohms, of depolarizing mix- ture per linear inch of a 1" column..... | .94 | 1.69 | 1.90 | .86 |
| Relative coherence of depolarizing mixture | 1.9 | 1.7 | 1.5 | 1.6 |

TABLE II

SCREEN ANALYSIS OF WASHED AND DRIED DEPOLARIZING
MIXTURES

| | A | B | C | D |
|-----------------------|------|------|------|------|
| On 20 mesh..... | 4.8 | 0.2 | 1.3 | 0.5 |
| 40 " | 25.5 | 12.8 | 20.0 | 29.0 |
| 60 " | 11.8 | 14.3 | 10.5 | 12.0 |
| 80 " | 4.3 | 5.3 | 7.0 | 3.3 |
| 100 " | 9.8 | 22.5 | 28.8 | 12.0 |
| 150 " | 2.3 | 7.3 | 8.5 | 4.5 |
| Through 150 mesh..... | 41.5 | 37.6 | 24.2 | 38.7 |

TABLE III

PERCENTAGE OF MnO_2 IN VARIOUS SIZES

| | A | B | C | D |
|-------------------|------|------|------|------|
| On 20 and 40..... | 74.9 | 71.5 | 82.5 | 60.3 |
| 60 and 80..... | 53.8 | 61.6 | 46.3 | 45.9 |
| 100..... | 45.2 | 38.3 | 27.1 | 41.8 |
| 150..... | 44.4 | 37.0 | 30.8 | 38.1 |
| Through 150..... | 31.3 | 38.3 | 50.2 | 31.7 |

TABLE IV

 NH_4Cl AND $ZnCl_2$ IN PAPERS AND MIXTURES

| | A | B | C | D |
|---|------|------|------|------|
| Grams NH_4Cl in papers, per cell..... | 10.1 | 13.4 | 12.3 | 12.3 |
| " NH_4Cl in mixture " " | 36.2 | 42.6 | 25.1 | 30.5 |
| " NH_4Cl , total, " " | 46.3 | 56.0 | 37.4 | 42.8 |
| " $ZnCl_2$ in papers, " " | 7.0 | 6.8 | 9.7 | 8.9 |
| " $ZnCl_2$ in mixture, " " | 13.8 | 10.3 | 15.8 | 15.5 |
| Total..... | 20.8 | 17.1 | 25.5 | 24.4 |

(Abstract)

SOME OBSERVATIONS ON BASE METAL THERMO-COUPLES

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The object of this investigation was to determine the variations in the electromotive forces of the following well known base metal couples when heated over different lengths and also after several heat treatments:—

Couple 6A—Nickel-chromium versus nickel-iron,

“ 7A—Nickel-iron versus nickel containing a little iron,

“ 18—Nickel-steel versus nickel containing a little aluminum,

“ 19—Nickel versus nickel-steel,

“ 20—Nickel-copper versus iron-manganese.

The couples were all new and were cut to lengths of about 18 inches. They were all compared one at a time against a standardized platinum couple in an electrically heated tube furnace and the indications of electromotive force of each couple during a test were taken on separate Leeds & Northrup Type K potentiometers. Five series of tests were made:—

- Series 1. All couples calibrated with lengths of 4 inches heated.
- “ 2. All couples calibrated with lengths of 15 inches heated.
- “ 3. All couples heated for 20 hours at 400°C. and then calibrated with 15 inches heated.
- “ 4. All couples heated for 24 hours at 600°C. and then calibrated with 15 inches heated.
- “ 5. All couples heated for 24 hours at 800°C. and then calibrated with 15 inches heated.

The tabulated results as taken from the curves of temperature versus electromotive force show that couples 6A, 7A, 19 and 20, do not indicate an error greater than 25°C. at 1000°C. when heated over 4 inches and 15 inches respectively. Couple 6A, however, undergoes a marked change after being heated at 800°C. and gives indications resulting in differences of over 100°C. at 35 millivolts. Couple 18 has a decided point of inflection which would introduce difficulties in arranging a scale for the indicating instrument.

Most of the couples are accurate to within 25°C. when immersed at different depths and after heating for extended periods of time, but some may introduce errors approximating 125°C. Caution should be used in purchasing and using these types of couples, and frequent calibrations should be made on accurate work.

| C° | Couple No. 6A | | | Couple No. 7A | | |
|------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| | Series 1 M. V. | Series 2 M. V. | Series 5 M. V. | Series 1 M. V. | Series 2 M. V. | Series 5 M. V. |
| 250 | | | | 4.8 | 4.5 | 4.8 |
| 300 | 10.2 | 10.9 | 10.0 | 5.7 | 5.5 | 5.7 |
| 400 | 14.4 | 14.8 | 14.0 | 7.7 | 7.4 | 7.7 |
| 500 | 18.5 | 18.8 | 17.8 | 9.7 | 9.5 | 9.7 |
| 600 | 22.5 | 22.6 | 21.5 | 12.1 | 11.9 | 12.1 |
| 700 | 26.6 | 26.3 | 24.8 | 14.9 | 14.5 | 14.9 |
| 800 | 30.5 | 30.1 | 28.0 | 18.1 | 17.7 | 18.1 |
| 900 | 34.3 | 33.8 | 31.1 | 21.5 | 20.8 | 21.5 |
| 1000 | 37.9 | 37.3 | 34.0 | 24.7 | 23.8 | 24.7 |
| 1100 | 41.4 | 40.4 | 35.6 | | | |

| | Couple No. 18 | | | Couple No. 19 | | |
|------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| C° | Series 1 M. V. | Series 2 M. V. | Series 5 M. V. | Series 1 M. V. | Series 2 M. V. | Series 5 M. V. |
| 250 | 7.1 | 7.1 | 7.1 | 6.0 | 6.2 | 6.5 |
| 300 | 8.4 | 8.4 | 8.0 | 7.1 | 7.3 | 7.6 |
| 400 | 10.2 | 9.3 | 9.5 | 9.2 | 9.3 | 9.8 |
| 500 | 11.4 | 10.1 | 10.6 | 11.4 | 11.7 | 12.1 |
| 600 | 12.8 | 11.5 | 11.9 | 13.9 | 14.1 | 14.7 |
| 700 | 14.7 | 13.1 | 13.5 | 16.5 | 16.8 | 17.3 |
| 800 | 17.0 | 15.0 | 15.4 | 19.3 | 19.7 | 20.4 |
| 900 | 19.5 | 17.1 | 17.7 | 22.5 | 22.9 | 23.7 |
| 1000 | 21.6 | 18.9 | 19.6 | 25.9 | 26.2 | 27.2 |
| 1100 | 23.9 | 20.9 | 21.5 | 29.3 | 29.6 | 30.7 |

Couple No. 20

| C° | Series 1 M. V. | Series 2 M. V. | Series 5 M. V. |
|------|-------------------|-------------------|-------------------|
| 250 | | | |
| 300 | 14.7 | 15.0 | 15.6 |
| 400 | 20.2 | 20.6 | 21.0 |
| 500 | 25.6 | 26.2 | 26.7 |
| 600 | 31.2 | 31.8 | 32.3 |
| 700 | 36.8 | 37.5 | 28.0 |
| 800 | 43.0 | 43.9 | 44.3 |
| 900 | 49.7 | 50.4 | 51.1 |
| 1000 | 55.2 | 55.9 | 56.5 |
| 1100 | | | |

REDUCTION OF IRON ORES IN THE ELECTRIC FURNACE

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Due to the large number of articles and papers which have appeared on this subject, the writer will assume that the reader is familiar with the history and evolution of the electric iron reduction furnace, and will in this paper therefore endeavor to deal only with those points which have been brought out as a result of the work which has been done up to the present time.

CONDITIONS FAVORABLE TO THE USE OF THE ELECTRIC REDUCTION FURNACE

In the first place, let it be clearly understood that the electric furnace was not developed with the idea of competing with the blast furnace, but only to permit of the smelting of ores in those localities where blast furnace practice is not commercially feasible, due to the high cost of charcoal or coke, as for instance in California or Canada. In Sweden, although the iron industry has been well established in that country for some hundreds of years,¹ the ores being smelted in charcoal blast furnaces, it has long been apparent to those familiar with the situation that some innovation would have to be introduced in order to enable the Swedish iron manufacturers to keep the cost of production down, for each year has seen an increase in the cost of charcoal, due to the fact that wood for making charcoal is becoming scarce owing to the depletion of the forests and the increased amount which is used for the production of wood pulp for the paper mills. It was these facts that caused the Swedish Engineers to turn their attention to the possibilities of electric smelting.

¹ Sweden: Its People and Its Industries; by Axel Gustav Sunbärg. Published by order of the Government, Stockholm, 1904.

IRON ELECTRIC FURNACE PLANTS BEING OPERATED AT THE PRESENT TIME

These are as follows:—

| | | |
|--|-----------------------|-------------|
| Trollhättan, Sweden | 1 furnace | 2,500 h.p. |
| Domnarfvet, " | 1 " | 3,500 " |
| Hagfors, " | 2 " at 3000 h.p. | 6,000 " |
| Hardanger, Norway | 1 " | 3,500 " |
| Heroult, Shasta Co., Cal. | 1 " | 2,000 " |
| while the following are nearing completion:— | | |
| Hardanger, Norway | 1 furnace (extension) | 3,500 h.p. |
| Arendal, " | 3 " at 3000 h.p. | 9,000 " |
| Switzerland " | 1 " | 2,500 " |
| Total furnaces built and building | | 30,500 h.p. |

The Noble Electric Steel Company at Heroult, Shasta County, California, are also installing additional furnaces of sufficient capacity to give an output of 100 tons of pig iron a day.

CHEMISTRY OF THE REDUCTION OF IRON ORES IN THE ELECTRIC FURNACE

As is well known, reduction of iron ores is effected by raising the ore and the reducing agent to such a temperature that a reaction takes place between the oxygen and the reducing agent, which in most cases is some form of carbon. As is also now known, iron ores for the most part, are at the present time reduced in the blast furnace. In order to get a clear idea of the difference between a blast furnace and an electric reduction furnace, let us first briefly note how the work of reduction and subsequent melting of the reduced iron and fluxes is brought about in the blast furnace.

The charge is first properly calculated and is made up of the ore (oxide of iron plus gangue materials) and fluxes (for combining with the gangue materials of the ore) in suitable proportions, to make a fusible slag, and the fuel which is needed to provide heat and which also acts as a reducing agent. This fuel is most generally coke or charcoal and contains practically no volatile mat-

ter. Before the tuyeres the larger part of the fixed carbon passes to CO, but whether it first passes through the CO₂ state and is then reduced to CO by incandescent carbon is still a debated subject. At any rate CO is the final product, and in its production a high enough temperature is produced to melt down the previously reduced iron, and to form a fluid slag from the fluxes and gange materials present, and it is just at this point that we may note the difference between the blast furnace and an electric reduction furnace, for in the electric furnace the heat necessary for performing the functions above mentioned, namely, the melting down of the iron and slag, is furnished by the electric current. In other words, the electric current is used to replace that portion of the fuel in the blast furnace which is necessary for the above mentioned purposes. In the blast furnace the amount of fuel necessary to produce the smelting temperature, and not the amount necessary for the reduction of the oxides, determines the amount of fuel that is used. In the electric furnaces, the amount of electric energy necessary for producing the smelting temperature is used in place of coke or charcoal and as only one-third or less of the coke that is used in blast-furnace work is needed for the reduction of the iron oxides, we are thus able to produce in the electric furnace three times as much iron with one ton of coke or charcoal as in a blast furnace, for in the latter case the coke or charcoal is used only as a reducing agent. Such being the case, let us now consider the amount of electrical energy and carbon that are necessary to produce one ton of pig iron in an electric furnace.

This problem has been carefully worked out by Lars Yngström,² Professor J. W. Richards³ and others, and hence it is not necessary in this connection to more than give the essential points in such a calculation.

In determining the amount of electrical energy necessary to produce one ton of pig iron from a given ore we have to calculate the amount of heat absorbed by—

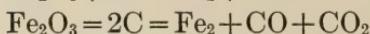
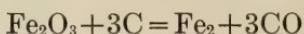
1. The reduction of the oxides to iron;
2. The reduction of the SiO₂ to Si;

² The Engineer (London), Feb. 26, 1910, page 206.

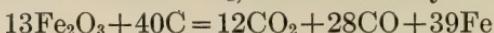
³ Metallurgical Calculations, by Jos. W. Richards; Part II, page 403.

3. The melting and superheating of N kg. of iron;
4. The melting and superheating of N kg. of slag;
5. The heating of X kg. CO₂ plus CO to whatever temperature it is determined that they should escape from this shaft.

From the number of calories absorbed in this manner we may deduct the heat that would be developed by the combustion of the X kg. of carbon needed for the reduction. The calculation of the latter, that is, of the amount of carbon needed for the reduction of the oxygen, is not an easy matter, for as has been pointed out by Professor Richards, in calculating the amount of carbon necessary to reduce the oxide of iron, we have no way of knowing what proportion of carbon will form CO and what CO₂, for the amount of each that will be formed depends upon the temperature, CO being almost the only product that is formed at a high temperature, while CO₂ is formed in increasing amounts as the temperature decreases, the reactions being represented as follows:—



From these equations we note that if the gaseous product of the reduction is all CO, not more than one-third as much carbon is required for the reduction as is in the case of blast-furnace practice. Yngström in his calculations assumes that when carbon combines with oxygen in the electric furnace, a mixture is formed which contains 30% (by volume) of CO₂, and on this basis calculates the carbon necessary for the reduction of the iron oxides present, and the subsequent development of heat by the formation of CO and CO₂, as is shown by the following equation:—



In his computations he uses the following theoretical values:—

To reduce 1 kg. Fe from Fe₃O₄ there are required 1650 calories

| | | | | | |
|---|---|--------------------------------|---|------|---|
| “ | “ | Fe ₂ O ₃ | “ | 1800 | “ |
|---|---|--------------------------------|---|------|---|

| | | | | | |
|---|----------|------------------|---|------|---|
| “ | 1 kg. Si | SiO ₂ | “ | 7830 | “ |
|---|----------|------------------|---|------|---|

| | | |
|--|------|---|
| By oxidation of 1 kg. C to CO ₂ there are developed | 7080 | “ |
|--|------|---|

| | | | | |
|---|----|---|------|---|
| “ | CO | “ | 2470 | “ |
|---|----|---|------|---|

| | | |
|--------------------------|-----|---|
| 1 kw. hr. corresponds to | 857 | “ |
|--------------------------|-----|---|

| | | |
|--|-----|---|
| 1 kw. pig iron requires for melting and superheating | 280 | “ |
|--|-----|---|

| | | |
|------------------------------------|-----|---|
| 1 kg. slag (monsilicates) requires | 595 | “ |
|------------------------------------|-----|---|

As a result of his calculations we find that for the production of one ton of pig iron containing—

| | |
|---------|-----|
| Carbon | 3% |
| Silicon | 1% |
| Iron | 96% |

Manganese, phosphorus, sulphur traces

made from a charge containing 60% iron in the form of Fe_3O_4 , and with the escaping gases containing 30% CO_2 there would be required 248 kg. of carbon or 292 coke and 1460 kw. hours, which would correspond to 4.4 tons of pig iron per h.p. yr. of 365 days.

The production of this amount of iron per k.w. yr. has not been attained in actual practice for according to the latest reports from Trollhättan only 3.94 tons are produced per kw. yr.

Having thus briefly stated the fundamental chemical principles upon which the reduction of iron is based let us now consider:—

1. Some of the difficulties that had to be overcome in order to bring the furnace up to its present stage of development.
2. Some of the problems which yet remain to be solved.

DIFFICULTIES THAT HAD TO BE OVERCOME

An inspection of Harmet's drawings and of practically every one else who has given their attention to the development of an electric furnace for the reduction of iron ores, shows that the first idea was to construct a shaft similar to a blast furnace shaft, and to then substitute electrodes for tuyeres. This looks all right on paper, but when it was tried out in practice it was found that the life of the furnace wall in the neighborhood of the electrodes was shortlived and no amount of water-cooling served to obviate this difficulty, but rather increased it if anything, due to jackets burning out, etc. etc. As was early observed by Heroult, the proper way to maintain the walls of an electric-furnace crucible is to get the electrodes as far removed from the side walls as possible, and in the development of the furnace in California and in Sweden it was found not only necessary to do this but also to keep the charge as far as possible from the roof of the crucible, for unless this was done the roof was shortlived, due

to the intense local heat which is generated at the point where the electrodes enter the charge. The maintenance of the roof of the crucible was one of the most serious difficulties that had to be overcome, and in overcoming this difficulty the present shape of the roof of the crucible and the manner in which the electrodes are introduced into the crucible was evolved. As a further protection to the roof of the crucible a part of the gases escaping from the top of the shaft were returned to the crucible in order to cool the same, as well as assist in the reduction of the charge.

THE ELECTRODE PROBLEM

Although the Swedish experimenters did not have so much to contend with in this respect, in California the difficulty in securing electrodes that would meet the requirements greatly interfered with the progress of the work. When the latter was begun in California the manufacturers of electrodes in this country had not previously been called upon to furnish electrodes of such large cross-section, namely, about 20 inches square and about 72 inches in length. Of those first furnished, that part of the electrode projecting into the crucible would either break off completely after it became heated up, or else large chunks would spall off from it, and as can be readily imagined these broken pieces gave no end of trouble in operating the furnace. That others also encountered this difficulty is evident from the following quotation from a paper presented by William R. Walker at the last meeting of the American Iron and Steel Institute:

“Our problems, mechanical, metallurgical and otherwise proved many, and our experience soon demonstrated that the conditions surrounding the successful operation of a large electric furnace were in many respects entirely different from those involved in the use of smaller units. In illustration, the demands of a 15-ton electric furnace proved to be far in advance of the art of manufacturing electrodes. Our necessities represented a requirement that the electrode manufacturers of America and Europe had not been called upon to meet, and it took much time and money before there was finally accomplished the 20-inch round amorphous carbon electrode and that is now being used at South Chicago.”

At the plant of the Noble Electric Steel Company it was finally decided to try graphite electrodes. These worked very satisfactorily in all respects except for the fact that on account of the angle at which it was necessary to insert them in the crucible, due to the manner in which the furnace was constructed, they were subject to a severe strain which caused them to break at the threaded joints. The electrode problem is, however, no longer a serious matter. As stated by Mr. Walker in his paper, the 20-inch round electrodes now in use at South Chicago give satisfaction, and the engineers at Trollhättan also report that the large carbon electrodes, of about the same size as those used at South Chicago, meet their requirements.

PROBLEMS YET TO BE SOLVED IN CONNECTION WITH ELECTRIC-FURNACE WORK

In this connection it may be well to first take up a discussion of the results which have been obtained at Trollhättan and in California.

A most careful record was kept of the work done at Trollhättan during the period November 15, 1910 to April 1911, and the data thus obtained was incorporated in a report which was submitted to Jern-Kontoret by two of its engineers, namely, Messrs. J. A. Leffler and E. Odelberg. A translation of the essential parts of this report was made by C. Dellwik and appeared in the London Iron and Coal Trades Review in June 1911. This report was also ably discussed by Mr. T. D. Robertson in a paper which he presented before the Toronto meeting of the American Electrochemical Society, September 1911. It is also the subject of a paper by Otto Frick which appeared in Metallurgical and Chemical Engineering for December 1911. In this paper Mr. Frick also discusses the results which were obtained in California, and for that reason it may be well to consider at this time some of the points brought out in this paper.

THE VOLUME OF THE SHAFT, AS COMPARED TO THE CAPACITY OF THE FURNACE

Theoretically the volume of the shaft of an electric furnace should be great enough to permit of the complete (practically) reduction of the ore before it enters the crucible. In other words, the ideal condition in electric reduction-furnace work would be to have the charge in such a condition as to only require melting by the time it comes in proximity to the electrodes. The writer is of the opinion that this as yet has not been done; that the degree of reduction that has taken place in the shaft of the electric furnace has varied all the way from nil up to a considerable percentage less than complete reduction. If we grant that the size of the shaft at Trollhättan has been properly calculated, and that the volume of charge in 24 hours to volume of furnace should be 1.55, then in order to insure the best economical working conditions of the furnace we have to turn our attention to the consideration of the reduction of the charge in the shaft.

REDUCTION IN SHAFT OF FURNACE

In an ordinary blast furnace the weight of the gases produced exceeds the weight of the charge by 30 to 50%, whereas in electric reduction-furnace work the gases evolved amount to only about 40% by weight of the charge. In other words, in the blast furnace in the production of one ton of iron there are three to four times as much gas given off as there is in the production of one ton of iron in the electric furnace. Moreover, the temperature of the gas as it leaves the tuyeres may be as much as 1600°C., whereas the highest temperature stated to have been attained at the lower end of the stack in the work at Trollhättan is 985°C. Even if this be granted, and that the temperature of the gas as it enters the stack may have as high a temperature as 1000°, as pointed out by Frick, "inasmuch as the weight of the gases produced is only 35 to 45% of the weight of the charge, the charge would not be heated to more than about 350°C, due to the fact that the specific heat of the gas and the charge are about the same. Thus, we see that we cannot expect complete reduction in the shaft if we depend solely upon the heat from the gases which are

generated in the regular manner. In other words, the shaft acts merely as a preheater, with possibly a small amount of reduction taking place therein, but for the most part reduction takes place in the crucible by means of solid carbon.

Thus we see that an electric furnace may be operated in one of two ways:—

1. Reduction of the ore in the crucible by means of solid carbon, with no attempt at reduction in the stack, as is done in California at the present time by the Noble Electric Steel Company.

2. Partial or complete reduction in the stack, this being the idea on which the Swedish furnaces are operated.

As we all know, that which may theoretically be best is not always so in practice. In this instance we are not able to judge by results, as we have not enough accumulated data at our disposal, and so can only look at the matter from a theoretical standpoint. In the reduction of any given iron ore we have to remove a definite amount of oxygen for every ton of iron made. Therefore, in the removal of this oxygen it would theoretically be best to remove it all in the form of CO. Due to the negative action of CO₂ gas at various temperatures, this is not possible, it having been determined by experimental work that the ratio of CO₂ to CO should not be greater than 1:1, 1:2 being the ratio in which they are usually present in blast furnace gases. The curves shown in figures 1 and 2 are the work of Prof. Richards. A study of the curves shown in figure 1 illustrates that in electric-furnace work the greater the per cent. of CO₂ in the gas the less is the amount of carbon required for removing the oxygen from the amount of ore necessary to produce one ton of iron. Figure 2 shows that the greater the amount of CO produced the greater is the amount of electrical energy necessary to produce one ton of pig iron. Therefore, if we are able to judge from the deductions which it is possible to make from these curves, we may say that the efficiency of the electric furnace will be increased as reduction is effected by the gases in the shaft, and that the aim should be to bring about a ratio of CO₂ to CO in the escaping gases of 1:1. If this be granted it would seem that reduction in the shaft is necessary, and if we accept the latter

statement there then arises the question of how best to bring it about.

The essential factors in accomplishing reduction in the stack are:—

1. Temperature;
2. Time;
3. Percentage of CO in gas.

As has just been pointed out, the volume of the gas generated by the reduction of the oxides is not sufficient to maintain a reduction temperature in the stack. As a remedy for this difficulty the present system of gas circulation was adopted, which system we will now briefly discuss.

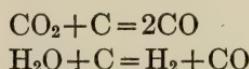
GAS CIRCULATION

As has been pointed out by Frick in his paper, the idea of using circulating gas in the electric furnace was conceived by Harmet and incorporated by him in his papers on the reduction of iron ores in the electric furnace.

At the present time gas circulation is used in the A. B. Elektrometall furnaces for the following reasons:—

1. To cool the superheated brickwork of the crucible;
2. To carry up through the stack a sufficiently large volume of gas which has been raised to a high enough temperature to bring about reduction in the stack. This method has been the subject of a great deal of discussion. At this year's April meeting of the American Electrochemical Society, Prof. Richards presented a paper on this subject. As stated by him, the objections to the circulation of the gas by the method at present employed are as follows:—

1. The moisture of the charge and the CO₂ of the flux and CO₂ gas naturally produced in the furnace are returned in a large part to the crucible, and react upon the unconsumed carbon by the reactions—



2. This very materially cools the smelting zone of the furnace, its most vital working part.

3. The system is cumbersome and expensive, and soon reaches the maximum of useful effect.

In order to overcome these objections Professor Richards proposed:—

1. To keep the ore in the shaft at a low-red heat;

2. Then allow the CO gas produced by reduction in the crucible to rise slowly up through the charge, and thus give to it, the best opportunity of producing the maximum amount of CO₂.

In the circulation of gas, as pointed out by Professor Richards, it is not the increased volume of the circulating gas that performs the reduction, it being quite evident that when the amount of gas passing through the furnace is increased two or three times its velocity is also increased to that extent, and therefore its contact with the ore is only one-half to one-third as long. Such being the case, the only value of circulating a portion of the gas escaping from the top of the shaft, so far as the problem of reduction is concerned, is that the charge in the shaft is kept at a temperature necessary for reduction, but on the other hand the CO₂ returned to the crucible is reduced by C to CO, and thus one aim of the electric furnace is defeated, namely, to remove the oxygen from the ore with a minimum amount of carbon.

Nevertheless, there are objections to the methods proposed by Professor Richards for obviating the difficulties connected with the present method of gas circulation which may be briefly stated as follows:—

1. The writer is of the opinion that it would be a difficult matter to successfully heat the charge in the stack by means of surface electrodes embedded in the walls of the shaft.

2. That at a low-red heat (say 480°C) reduction takes place very slowly, and hence the volume in the shaft would have to be very large in order to give the charge time enough in passing through the shaft to be reduced.

3. That the use of burnt limestone, where shaft reduction is attempted, would introduce an unnecessarily large amount of fines into the charge.

4. That water-cooled plates in the arch of the crucible, while

a benefit, would not of themselves offset the benefit derived from the introduction of cold gas beneath the roof of the crucible.

Naturally if simplicity can be combined with efficiency in a metallurgical process, so much the better, and so in this case, as stated by Mr. Leffler in his discussion of Professor Richards' paper, if gas circulation could be dispensed with, nobody would like it better than those who have to run the furnace, and they are quite ready and willing to be shown how to do it if some one will bring forward a method which their experience in operating electric furnaces does not show them to be impractical.

OTHER SUGGESTED IMPROVEMENTS

1. *Calcining of limestone outside of furnace.* This has been repeatedly suggested, because theoretically it seems the proper thing to do, but as stated by Mr. Leffler in his reply to Mr. Frick's paper, they have not found it practical to do so, because, among other things, it causes the burden to hang. The writer is of the opinion, as previously stated, that it would also introduce an exceedingly large amount of fine material into the charge. He believes that if reduction is not attempted in the shaft, as is the case at present in the California practice, the calcined limestone may be advantageously added to the charge.

2. *Preheating of the ore.* Judging by experience gained in California in regard to this matter, the writer is of the opinion that the preheating of the charge is beneficial, for the following reasons:—

(a) It dries the charge and thus permits of a more accurate weighing into the shaft of ore, fluxes and carbon.

(b) The initial temperature of the charge on entering the stack is thus sufficiently high to permit of its at once being reduced.

3. *The smelting of the fine ores.* The writer is privileged to quote from a communication which he has just received from Electro-Metals, Limited, in regard to this matter:—

"As was explained in our first publication on this subject, the object of this plant (at Trollhättan) was to determine the relative merits of electric smelting as compared with ordinary blast-furnace smelting. For this reason the work has been carried out

under widely varying conditions, and with different kinds of ore and fuel. In consequence the results are by no means uniform and scarcely suitable for conclusions based on the average figures.

One object of some importance in Sweden was to determine the proportion of ore concentrates which could be used. The results prove that a large proportion of concentrates is detrimental to smooth running and good results.

This is readily understood from the fact that only about one-third as much charcoal is used as in the blast furnace, and concentrates therefore have an increased tendency to choke the passage of the gas."

As will be seen from the above, it is not feasible to use a large proportion of fines in making up the charge for the electric furnace. This, however, does not prevent the smelting of fine ores, for they may be sintered.

The advantages derived from sintering in electric-furnace work would be as follows:—

1. The agglomeration of the fines, which is beneficial in two respects, namely:—

(a) The bringing together of the fines into lumps of such size as to permit of easy passage of the gases up through the charge in the shaft.

(b) The bringing of the fines together into a porous lump, the physical condition being especially suited to reduction by gases.

2. The advantages derived from preheating; that is, the hot sintered ore could be charged direct into the shaft and thus be at a temperature to be at once reduced.

4. *The size of the unit.* The electric reduction furnaces now in operation vary in size, as regards their horsepower, from 1500 up to 3500, while the largest yet designed by A. B. Elektrometall, (of Sweden) is 7,500 kw. As can be readily understood, it is quite important that the size of the unit be made as large as possible, and the writer is of the opinion that no one is prepared to say at the present time just what that size will ultimately be.

5. *Efficiency of the furnace.* The efficiency of the furnace will also be increased as time goes on, and probably by improvements along the following lines:—

- (a) The utilization of the waste gases;
- (b) The securing of a high-power factor;
- (c) The correction of induction losses;
- (d) The further study of the single-phase furnace vs. the 3-phase furnace.

As regards the latter, inasmuch as practically all large power installations are 3-phase, it would seem that the only logical thing to do is to use 3-phase current in electric-furnace work, but from data submitted by Catani¹ it would seem as if the mono-phase furnace is more efficient than the poly-phase furnace.

THE ELECTRIC FURNACE AS COMPARED TO THE BLAST FURNACE

As has been stated in the first part of this paper, the electric furnace was not evolved in the hopes of competing with the blast furnace, but of finding a furnace and a process which would be able to produce iron in those localities where blast-furnace practice was not feasible; or, as in Sweden, where the cost of blast-furnace fuel was becoming so great as to cause the existing blast-furnace practice to become prohibitive.

Broadly speaking, we may say that the smelting of iron ores in an electric furnace depends upon the relative costs of either charcoal or coke, and of electric power. As regards the latter, it must be cheap. As is well known, electric power at the present time can be developed much more cheaply than it could when Captain Stassano² made his experiments in 1898, and it will probably be produced much more cheaply in the future. However, it is not the purpose of the writer to speculate on this point but to state the facts as he understands them. As has been previously pointed out in this paper, the average consumption of charcoal or coke in the electric furnace in the production of one ton of pig iron is about one-third of what it is in the blast furnace. Hence, as has been pointed out by Knesche³, when we take into consideration the consumption of electrodes, the saving is prac-

¹ Trans. Am. Electrochem. Soc., Vol. XV, p. 168.

² Stassano-Steel Furnace. Electrochemist and Metallurgist—Vol. 1 (1901) p. 230; Electrochemical Industry—Vol. 1 (1902-03) pp. 247, 363.

³ Iron Trade Review, Jan. 5, 1911, p. 65—Electric Smelting of Ore in the United States, by J. A. Knesche.

tically .7 of a ton of coke or charcoal per ton of iron produced, as compared to blast-furnace practice. Let us suppose that we have a case where coke costs six dollars a ton, and a kw. yr. costs sixteen dollars. From the report of the work done at Trollhättan,¹ we find that on an average 2225 kw. hrs. were required to produce one ton of pig, or that 3.94 tons of iron were produced per kw. yr., and if a kw. yr. costs \$16 the cost per ton of pig iron for power would be \$4.00 to which must be added the cost of .3 ton of coke, and likewise the cost of about 12 lbs. electrodes, or a total cost which is shown as follows:—

| | |
|-----------------------------------|--------|
| 2225 kw. hrs. at \$16 kw. yr..... | \$4.00 |
| .3 ton of coke at \$6..... | 1.80 |
| 12 lbs. electrodes at \$.06 | .72 |
| | — |
| Total | \$6.52 |

As 1 ton of iron can be produced in a blast furnace from 1 ton of coke, the respective costs in the blast furnace and in the electric furnace would be \$6.00 and \$6.52. Hence, if considered on this basis alone, the electric furnace, with coke at \$6.00 per ton and power at \$16.00 per kw. yr., could not compete with the blast furnace. There are, however, other items to be taken into consideration besides those given, such as initial cost of plant, quality of iron produced, and especially the efficiency of the furnace, for, as has been pointed out by Ashcroft,² "the efficiency of many non-electrical furnaces is barely 10% of the theoretical, and very few will exceed 25%, while the efficiency of electrical appliances sometimes reaches 75% and is often 50%."

Hence, with no greater difference than shown above between the respective costs, a careful investigation of all items which enter into the total cost of a ton of pig iron, as well as the nature of the ore to be treated, the grade, product desired, etc., might readily result in disclosing the fact that it would be more profit-

¹ Fortsatt Redogörelse För Jernkontorets Försöksverk I Trollhättan Af J. A. Leffler och E. Nyström, Stockholm, 1912. Electric Furnace Pig Iron at Trollhättan. Metallurgical and Chemical Eng., July 1912. p. 413.

² The influence of cheap electricity on electrolytic and electro-thermal industry. Trans. Faraday Soc., Vol. IV, pp. 134-142.

ble to produce pig iron in the electric furnace than in the blast furnace, even with the margin above stated in favor of the blast furnace. There are, however, very few localities where coke costs only \$6.00 a ton if the cost of an electrical kw. yr. is \$16. More often the cost of coke in such districts is \$12 to \$14, and with coke at these figures the advantage is decidedly with the electric furnace, with power at \$16 a k. w. yr.

COST OF POWER

Hydro-electric power

In the development of electric power by waterpower the gross cost to the consumer depends upon the initial cost of installation, while the latter in turn depends, among other things, upon:—

1. Mean average flow of water for 12 months;
2. Whether expensive reservoirs must be constructed;
3. Whether these reservoirs are situated a long distance from the power-plant, and so necessitating the construction of long ditches, flumes, tunnels, or pipelines.
4. Whether expensive dams have to be constructed, etc.

In all the waterpowers which are available we find perhaps either one or all of the above mentioned prerequisites have to be met and dealt with, and that the cost of installation may be as low as \$35 per e. h. p., or as high as \$300 per e. h. p. The writer is informed that the installation at Niagara Falls could not have cost less than \$150 e. h. p., as have also some of the installations in California. At Ottawa, Canada, the cost of installation must have been very reasonable as the writer has recently seen a communication from a commissioner in that city in which he states that they are prepared to furnish large amounts of electrical energy at a cost not to exceed \$10 per e. h. p.

Power produced by gas engines

Mr. J. A. Knesche¹ has very carefully gone into the subject of the production of electric power from other sources than water-power, and it may be well in this connection to note his conclusions in regard to the same. He assumes:—

¹ Iron Trade Review, Jan. 5, 1911, p. 65.

1. That 100 tons of iron are to be produced a day.
2. That one-third h. p. y. is required per ton of pig produced.
3. That 8400 h. p. hrs. constitute 1 h. p. y.
4. That, based upon the above assumptions, with necessary reserves in the producers and engines, that an installation of 15,000 h. p. would be required to produce 100 tons of pig iron per day.

By careful working out of the details he finds that if this power be produced by gas engines from gas produced in a by-product gas-producer plant, the total cost will be \$95 per h. p. of completed plant, and that if the producing power be charged (for the entire power-plant) with salaries, wages, cost of fuel (coal at 65 cents per ton), water, lubricants, repairs on the entire equipment, and fixed charges (15%), and credited with the sale of the by-products, power can be delivered at the electric furnace for \$24.65 per h. p. y. These figures are summarized by Knesche in the following table:—

*Resumé of the different items entering into the cost of the h. p. year
at electric smelting furnace*

| | |
|--|--------------|
| Fixed charged on entire producer power plant | \$214,000.00 |
| Water | 15,750.00 |
| Oil, grease, waste, etc. | 24,600.00 |
| Wages and salaries in engine house | 26,850.00 |
| Repairs | 25,000.00 |
| Fuel | 42,850.00 |
| Wages at producers, boilers, ammonia plant, handling and shipping of ammonia | 29,200.00 |
| Sulphuric acid, lubricants, light, wages, and materials for repairs at producers and ammonia plant | 28,500.00 |
| | \$406,750.00 |
| Sulphate of ammonia | 147,800.00 |
| | \$258,950.00 |
| Total remaining costs | \$258,950.00 |
| Cost per horsepower-year at electric furnace | 24.65 |

In the above calculations Knesche assumes that the h. p. hr. at the furnace will be generated on 1.5 lbs. coal. He also estimates that 2,210 tons of sulphate of ammonia, as a by-product, would be obtained from the operation of the producer plant. However, this calculation does not take into consideration the gas that would be available for power purposes that would be produced in the operation of the electric furnaces, which Knesche shows would be as follows:—

Using Catani's estimate of 30,600 cubic feet as being the amount of gas given off in the electric furnace during the production of one ton of pig, in the production of 100 tons in 24 hours, there will be given off 63,750 cubic feet from which if we deduct 5% for unavoidable losses would leave 60,500 cubic feet, which would be equivalent to 1,000 e. h. p., from which if we deduct 200 h. p. hrs. for power purposes (other than furnace work) around the plant, would leave 800 h. p., and if the cost of power be credited with this amount the cost of the h. p. yr. could be brought down to about \$22.50.

Although this is considered a low figure for power produced in this manner, it is nevertheless costly power for electric reduction-furnace work. The writer knows of no place in the United States where electric power is produced by means other than water-power at this figure. It is perhaps possible to do so, and in an article by Carl Heinz¹ it is stated that with a peat-gas-producer of the Goerlitzer Maschinenbauanstalt, and with peat at a cost of \$1 per ton, power can be produced at the switchboard at a cost of 0.15 cent a kw. h.

Below is given a list of a few of the best articles and publications which have appeared on this subject:

ARNOU, C. L'état actuel de l'electrosidérurgie. Nouveaux procédia. Fours à résistance et à arc; caractéristiques électriques. Role. Avenir. Statistique. Lumière Elec., Oct. 1910.

BENNIE. Electric furnace—its place in Siderurgy. Jour. Can. Mining Inst., 1910, vol. XIII; Proc. Engrg. Soc. W. Pa., Jan. 1911.

¹ Stahl und Eisen, Aug. 17, 1911, p. 1359; abstracted in Metall. Chem. Eng., May 1912, p. 283.

CARCANO. The Production of Pig Iron at the Electric Furnace and the Industrial Utilization of Pyrite Residue. *Elec. & Metall. Ind.*, April 1909.

CATANI, R. Application of Electricity in the Metallurgical Industry of Italy. Paper read before Iron and Steel Institute. *Can. Mining Jour.*, 1911, p. 654.

FRICK. The Electric Reduction of Iron Ores. *Metall. Chem. Eng.*, Dec. 1911, p. 631. (Replied to by Leffler, *Metall. & Chem. Eng.*, Feb. 1912).

HAANEL, E. Report of Commission Appointed to Investigate different Electrothermic Processes for Smelting Iron Ores and Making Steel in Europe, 1904, Interior Dept., Canada. Report on Experiment at Sault Ste. Marie, Ontario, under Government Auspices, in Smelting on Canadian Iron Ores by Electrothermic Processes. 1907. Canada-Mines Branch, Interior Dept.

Report of the Investigation of an Electric Shaft Furnace, Domnarfvet, Sweden, etc. 1909. Interior Dept., Canada. Bull. 3, Dept. of Mines, Mines Branch, Interior Dept., Ottawa, 1910.

HÄRDËN, J. Smelting Iron Ores in Electric Furnaces in Comparison with Blast Furnace Practice. *Electrochem.-Mettal. Ind.* Jan. 1909.

KNESCHE, F. A. Electric Smelting of Ore in the United States. *Iron Trade Review*, Jan. 5, 1911.

RICHARDS, J. W. The Electrothermic Production of Iron and Steel. *Jour. Franklin Inst.*, Dec. 1907. Jan. 1908.

The Electric-Furnace Reduction of Iron Ore. *Iron Trade Review*, May 13, 1909; *Eng. News*, May 20, 1909.

Electric Reduction of Iron Ore. *Jour. Franklin Inst.*, Feb. 1910.

The Electrical Revolution in the Iron and Steel Industry of Norway and Sweden. *Proc. Eng. Soc. W. Pa.*, May 1911.

STANSFIELD, ALFRED. Production of Pig Iron from Iron Ore, Carbon, and Fluxes. *Canadian Eng.*, Dec. 1906.

Laboratory Experiments on Removing Sulphur and Phosphorus in Smelting Iron Ores. *Jour. Canadian Min. Inst.*, 1907.

STOUGHTON, BRADLEY. Notes on Electrothermic Manufacture
of Iron and Steel. *Jour. Franklin Inst.*, Feb. 1909.

YNGSTRÖM, LARS. Electric Blast Furnace at Domnarfvet,
Sweden. *Metall. & Chem. Eng.*, Jan. 1910.

Electric Production of Iron from Iron Ore. Report on Ex-
periments at Domnarfvet Iron Works. *Engineer, London*,
Feb. 25 and March 4, 1910.

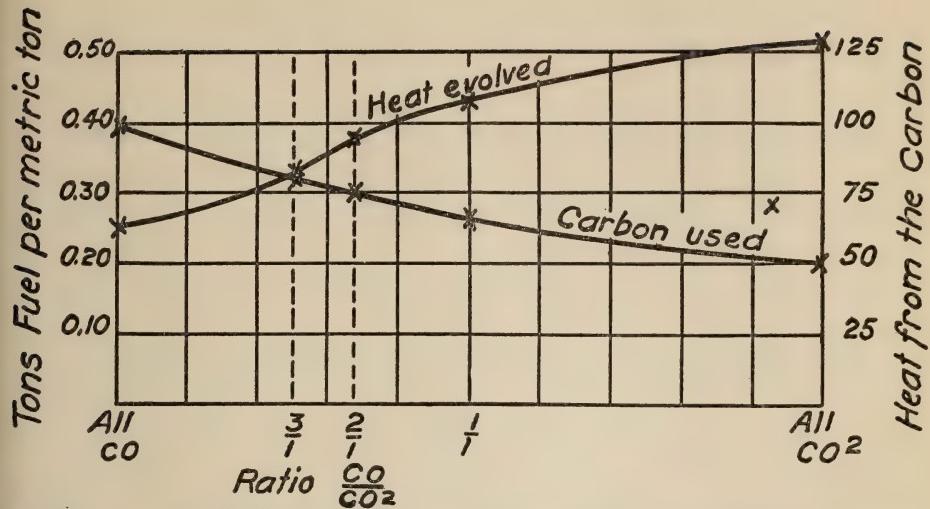


Fig. 1. Variation of Fuel Required and Heat Evolved with Composition of Waste Gases Produced.

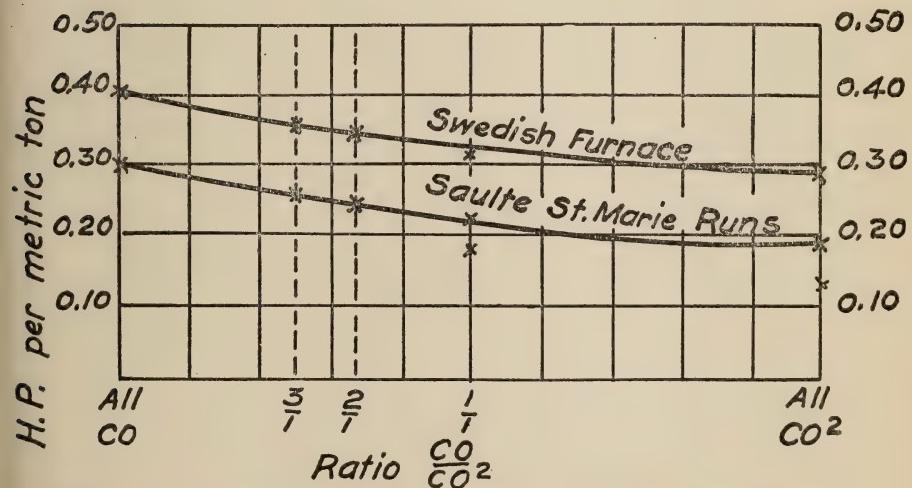


Fig. 2. Variation of Power Required with Composition of Waste Gases Produced.

ON THE METHOD OF PRODUCING BICALCIC PHOSPHATE WITH THE HELP OF ELECTROLYTICALLY PRODUCED ACID AND ALKALI

PROF. W. PALMAER

In order to meet the ever growing demand of agriculture for phosphate fertilizers, chiefly the following preparations are at present produced:

acid phosphate
basic slag
bone meal
bicalcic phosphate

which are here given in the order corresponding to the amount produced, acid phosphate being the phosphate fertilizer most largely produced, the annual output amounting to about 10,000,-000 tons.

Bicalcic phosphate so far has been produced only in small quantities, the production in Germany and France, for instance, during 1900, amounting to about 5,000 tons for each country. To date this product has been obtained only as a by-product in the manufacture of glue, i. e. in the process when bone is soaked in diluted hydrochloric acid, whereby the main product in the manufacture, the glue substance, remains undissolved, while a solution of bone phosphate is obtained as a by-product. This is turned to account by precipitation with lime, by which means bicalcic phosphate is obtained.

On the other hand it is a long while ago since it was first proposed to obtain bicalcic phosphate as the chief product from every kind of raw phosphate in the same way, viz., by extracting the raw phosphate with hydrochloric acid and precipitating the solution thus obtained with lime. This method would have the advantage that one could make use of very poor and otherwise valueless raw phosphate, provided it does not contain too large a proportion of any useless, soluble compound, such as car-

bonate of lime. In the production of acid phosphate, on the other hand, one can not utilize raw phosphate with a lower percentage than about 50% bone phosphate, since owing to the admixture of gypsum the percentage in the acid phosphate of available phosphoric acid is only about half that of the raw phosphate's percentage of phosphoric acid, and consequently consideration of freight charges for the preparation article excludes the use of a raw material in which the percentage is low.

However, it has been found that the price of hydrochloric acid has been too high for the adoption of this method. This in its turn is due to the fact that the production of hydrochloric acid according to the old methods entailed the sacrifice of sulphuric acid.

But the case is different if the acid is produced in such a way that a suitable salt, for instance perchlorate of sodium, is electrolyzed with a diaphragm, so that free acid is generated in the anode chamber, and a solution of caustic alkali in the cathode chamber. With an electrolyzing tension of $4\frac{1}{2}$ volts and 80 % current efficiency it is easy to calculate that in order to produce the Kilogram equivalent of acid 182 horse-power hours are required, whereby the alkali necessary for the precipitation of the bicalcic phosphate is obtained at the same time without additional cost in the cathode chamber. If we assume that 1 electric horse-power can be obtained for \$10 a year—the usual price in many parts of Europe and presumably in many places in America—then the cost of the equivalent of 1 Kilogram of acid amounts to about 24 cents, the alkali being obtained at the same time; while with the old method lime had to be purchased. There is no outlay for material beyond what is caused by spilling &c., as the electrolyte regenerates, as will be seen from what follows.

If we assume that the price of 1 ton of chamber acid with 65% H_2SO_4 is \$5, we shall find that the cost of the Kilogram-equivalent of H_2SO_4 (49 Kg.) is about 38 cents.

This calculation consequently shows that provided the remaining outlay for the elektrolytic process can be kept within reasonable limits, it should be assured of success, especially as it allows of the utilization of otherwise valueless raw phosphate or refuse.

This calculation was the basis of my investigations, the object of which was consequently to try to make the method economically feasible, chiefly by finding a suitable electrolyte, and by constructing a serviceable electrolyzer.

As in the process there is no consumption of chemicals, beyond loss by spilling, &c., the cost of the sulphuric acid used in producing acid phosphate is replaced by the cost of the electric power. The economic result of the method depends therefore in the first place on the price of the power.

Before entering upon detailed descriptions, a general survey of the method will be of advantage.

I. GENERAL FEATURES OF THE METHOD

In an apparatus expressly constructed for the method, a solution of chlorate or perchlorate of sodium is electrolyzed. In the anode chamber an acid is thereby generated—chloric or perchloric acid—and in the cathode chamber a solution of caustic soda. The electrolysis is continued until a certain quantity of the dissolved salt has been separated into acid and alkali. The anode and the cathode solutions are led off into separate receivers. The acid anode solution is then allowed to work in a dissolving battery upon raw phosphate, in which process the phosphate is dissolved. Into the solution thus obtained the alkaline cathode solution is introduced, the whole being meanwhile kept vigorously stirred, until the liquid bears evidence of a slightly acid reaction; to obtain that result about half the cathode solution is required. In the process bicalcic phosphate is precipitated as a finely crystalline precipitation, which is drained off by filtration and washed. The filtrate, which contains $\frac{1}{3}$ of the lime originally dissolved, but hardly any phosphoric acid, now has added to it the remainder of the cathode solution, which has previously been saturated with carbonic acid from fuel-gas. The lime is precipitated as carbonate, which is allowed to settle. The solution remaining above it is then drawn off. The original electrolyte is regenerated by its means and again enters the electrolyzing apparatus.

Of course, the hydrogen, obtained as a by-product at the cath-

ode in the electrolysis of the salt solution, could be used for making ammonia or in any other way thus increasing the value of the products obtained.

II. THE NATURE OF THE ELECTROLYTE

With reference to the electrolyte, the salt used should be of such a nature that its acid may yield, in conjunction with lime, an easily soluble salt, and of a kind which is not subject to change during electrolysis.

As electrolytes, solutions of perchlorate of sodium or chlorate of sodium are suitable, or else mixtures of those salts, the presence in small quantities of other salts, for instance chlorides, being of no account. Both these salts can now, since they are being produced by electrolysis, be had at reasonable prices. Nitrate of sodium cannot be used, because it is too strongly reduced at the cathode to nitrite, ammonia, etc.

Perchlorate of sodium is an ideal electrolyte for the purpose in question. On electrolyzing its solution with a diaphragm, sodium hydrate is formed in the cathode chamber and perchloric acid in the anode chamber, while hydrogen is developed at the cathode and ozonic oxygen at the anode. No noticeable reduction of the salt occurs at the cathode, nor any other change, and the solution of perchloric acid obtained is perfectly constant at such temperatures as occur in the electrolyzing (maximum 50°C.). Furthermore, the salt is exceedingly easily soluble (deliquescent) and thus easy to wash away.

Chlorate of sodium is less constant, in that the chloric acid solution formed in the anode chamber already begins to decompose at 40°C., free chlorine being developed. Moreover, it is considerably reduced at the cathode to chloride. But the principal change is that the development of oxygen at the anode almost ceases, because the chlorate there is oxidized to perchlorate. For this reason a start can very well be made with chlorate of sodium, since though the drawbacks mentioned (the decomposing of the chloric acid and the reduction of chlorate) appear at first, they soon disappear, viz., when the chlorate has become perchlorate of sodium. Even if you begin with chlorate of sod-

ium, the electrolyte consists after a while of pure perchlorate, which, as has been said, suffers no further change.

The loss of perchlorate of sodium by spilling and incomplete washing need not, according to our experience, be estimated higher than at about 1 % of the weight of the bicalcic phosphate developed.

Another way of carrying out the process is this:—A solution of chloride of sodium is electrolyzed so that a solution of caustic soda and free chlorine is obtained. The chlorine is transformed in the usual way into hydrochloric acid wherewith the raw phosphate is dissolved, whereupon a precipitate is formed with this caustic soda. The salt is then regenerated as before. Although common salt is cheaper than perchlorate of sodium or chlorate of sodium, the process, by several reasons (depreciation of anodes, losses of chlorine, etc.), is not so advantageous.

III. THE ELECTROLYSIS

The electrolysis of the perchlorate of sodium solution must be carried out, as has been mentioned, in a diaphragm apparatus, and it is clear that the problem is to find a suitable anode and a suitable diaphragm. Both difficulties have been solved in a perfectly satisfactory manner, but for the present I cannot enter into details.

The voltage has been found to amount on the average to 4.5 volts per cell, including loss in connections. It varies somewhat, depending on the age of the diaphragms, the efficiency of the electrical contracts and the temperature of the solutions, which may vary at different times of the year; but as stated, the average voltage is 4.5. The polarisation amounts to 2.97 volts.

In a diaphragm process, where the new substances formed at the cathode and the anode remain in the solution (in this case alkali, or perchloric acid), the current efficiency continually diminishes, of course, in proportion as the newly formed substances begin to take part in the current-circuit. We generally produce solutions with 1 gram—equivalent of acid or alkali per liter, and have then a current efficiency of 82% and a ballast of undecomposed salt in both acid and alkali solutions.

IV. THE RAW MATERIAL AND ITS UTILIZATION

Of course the high-percentage raw phosphates used to make acid phosphate can be employed for the process, but it is not for such, but rather for low-percentage raw phosphates, at present worthless or of inferior value, that the process is primarily designed. Here I need only mention in illustration low-percentage apatites and apatite waste, waste from magnetic separation of phosphoric iron-ore, and certain low-percentage phosphorites.

As the process consists in dissolving the bone phosphate occurring in raw phosphate, and then precipitating bicalcic phosphate from the solution, the product obtained will always be of the same nature, irrespective of the percentage of the raw phosphate. We have employed raw products whose percentage of bone phosphate varied between 20% and 88%.

Furthermore the raw phosphate need not be finely pulverised, provided that the bone phosphate is not embedded in insoluble minerals and that other soluble substances, such as certain silicates, do not occur in too great a quantity;— we have worked with material of as coarse crushing as 5 cm.

Assuming that the solution of bone phosphate is effected according to the formula $\text{Ca}_3\text{P}_2\text{O}_8 + 6\text{HClO}_4 = 3\text{Ca}(\text{ClO}_4)_2 + 2\text{H}_3\text{PO}_4$ then per liter of 1—normal acid 23.7 grams of phosphoric acid should be dissolved. It can be foreseen, however, that the reaction, in contrast, for instance, to the reaction $\text{Ca CO}_3 + 2\text{HClO}_4 = \text{Ca}(\text{Cl O}_4)_2 + \text{H}_2\text{O} + \text{CO}_2$ will not proceed quantitatively, since phosphoric acid is a much stronger acid than carbon anhydride. We have also found that we must reckon with a somewhat lower figure, say 20 gr. P_2O_5 or 43.6 gr. $\text{Ca}_3\text{P}_2\text{O}_8$ per liter of 1—normal acid. This figure holds good provided that no other bodies soluble in acids occur in the raw phosphate.

Of such, in the first place, we must take into consideration calcium carbonate, for, as we know, it readily and completely dissolves in acids. As the equivalent weight for phosphate acid (P_2O_5) is 23.7, and for carbon anhydride (CO_2) 22, we can consequently state that 1% of CO_2 in the raw phosphate causes approximately the same consumption of acid (or of energy) as 1% of P_2O_5 , without giving any product of any value to speak of (the

amount of carbonate of lime obtained as a by-product will of course be correspondingly greater). A raw phosphate which contains 20% of P_2O_5 (as $Ca_3P_2O_8$) and 2% of CO_2 (as $CaCO_3$) consequently requires about 10% more energy than a raw phosphate with the same proportion of phosphoric acid, but free from carbonate of lime.

Iron oxides (iron-ores), on the other hand, are only dissolved very slightly. We found that after 24 hours' shaking at the usual temperature with 1—normal acid, there was dissolved of magnetite a quantity corresponding to 0.24 grs. Fe_2O_3 per liter of hematite a quantity corresponding to 0.20 grs. Fe_2O_3 per liter which amounts are of no practical importance.

Most silicates are, as we know, insoluble in diluted acids. However, silicates may occur, for instance together with apatite, which are easily soluble that they dissolve to a noticeable degree if the acid is in contact with them for any length of time after most of the phosphate is dissolved. Attention must be paid to this in the course of the lixiviation, and the work regulated accordingly.

As regards the utilization of the bone phosphate in the raw material, we can as a rule count upon extracting 98% of it, sometimes more, sometimes a little less, viz., when easily soluble silicate is present.

V. PRECIPITATION OF THE BICALCIC PHOSPHATE AND CALCIUM CARBONATE

To precipitate the bicalcic phosphate we made use, as before stated, of the solution of caustic soda obtained by electrolysis and saturated afterwards by carbonic acid, which is introduced into the phosphate solution by means of a sprayer.

The employment of the soda solution as a precipitator, instead of lime-white, has a considerable advantage. For the fact is that as soon as the solution has become alkaline at any point, bone phosphate is precipitated there instead of bicalcic phosphate. This once precipitated bone phosphate is only slowly converted into bicalcic phosphate, even if the average acidity of the liquid is such that only bicalcic phosphate ought to occur. At least a

portion of the bone phosphate thus formed remains therefore in the precipitated bicalcic phosphate. The bone phosphate thus precipitated is very finely distributed, it is true, and is even soluble after drying in 2% citric acid; but it has no manuring value worth speaking of. The phosphoric acid precipitated as bone phosphate, must therefore be looked upon as lost.

Now it is clear that it would be much easier to avoid the formation of bone phosphate if a sodium hydrate solution, distributed in jets, were employed as the precipitator, than if lime-white were used, since in the latter case we get particles of solid calcic hydrate, round which the solution easily becomes alkaline.

Experience also proves that in employing sodium hydrate, which is added until the phosphate solution is still very slightly acid or only just neutral, bicalcic phosphate can be precipitated so completely that only 0.1 to 0.2% of all the phosphoric acid remains unprecipitated, while 98% of the phosphoric acid in the bicalcic phosphate is soluble in citrate, and thus only 2% of the phosphoric acid is present as bone phosphate.

The precipitated bicalcic phosphate, which is microcrystalline, is filtered off, washed and dried. It thus forms a light, pure white powder, and its proportion of citrate-soluble phosphoric acid amounts to from 35-38%, according to the completeness of the drying.

If we call to mind that about 2% of the phosphoric acid in the raw phosphate is left behind in the extraction, that no quantity to speak of remains unprecipitated, and that about 2% is recovered as precipitated bone phosphate, we shall find that about 96% of all the phosphoric acid in the raw phosphate is extracted in the process as valuable citrate-soluble phosphoric acid.

The bicalcic phosphate obtained shows, even if it contains iron and aluminum phosphate, no retrogradation of soluble phosphoric acid, which is simply due to the fact that it can be perfectly dried, after which no conversion can take place. On the other hand, as we know, retrogradation shows itself in damp acid phosphate. The following analyses may be quoted to show that retrogradation does not occur:

| | Total P ₂ O ₅ % | Citrate-soluble P ₂ O ₅ % | Citrate-soluble P ₂ O ₅ in % of total P ₂ O ₅ |
|----------------|--|--|---|
| fresh | 35.45 | 34.58 | 97.54 |
| after 3 months | 36.02 | 35.13 | 97.53 |
| " 6 " | 36.54 | 35.72 | 97.75 |

From the filtrate of the bicalcic phosphate is precipitated, as we have already mentioned, the lime that remains in the solution, together with the rest of the sodium hydrate solution, after the latter has been saturated with carbonic acid from fuel-gases, as carbonate of lime, which can be used as a fertilizer or in chemical work-shops.

Its mass corresponds to about $\frac{1}{4}$ of the weight of the bicalcic phosphate obtained, if the raw product used be free of carbonate. If calcium carbonate occurs in the raw product, the mass obtained in the process will be proportionately increased.

VI. POWER EXPENDITURE

From the statements given above, it is easy to calculate what electric horse-power (direct current) produces per year of $350 \times 24 = 8400$ hours; it will work out at 2.24 tons of bicalcic phosphate with 35% of citrate-soluble phosphoric acid, if free of carbonate. If a 38% article is produced, $\frac{2.24 \times 35}{38} = 2.06$ metric tons per horse-power year will be obtained, etc. The production with carbonaceous raw product has been stated above.

VII. VALUE OF BICALCIC PHOSPHATE FERTILIZER

Careful experiments extending over many years have been made, partly by Professor *H. G. Söderbaum*, Agricultural Chemist at the Central Institution for Experimental Agriculture, Stockholm, partly by Dr. *Hj. von Feilitzen*, Director of the Swedish Peat Society, Jönköping, Sweden. Professor Söderbaum's earlier investigations are reported in "The Experiment Station Record," edited by the U. S. Department of Agriculture, Washington,

Vol. XIV., No. 10, pp. 951-2 (1903), and he has also summed up the result of his investigations under the title of "Vegetationsversuche mit gefälltem Calciumphosphat" in the "Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich 1908, pp. 506-510. Dr. von Feilitzen has communicated the chief results of his investigations in the "Journal für Landwirtschaft," 1910, pp. 33-43.

As Dr. von Feilitzen is going to give an account of his further investigations at the Congress, I will here only briefly mention the chief result of his and Professor Söderbaum's culture trials.

The result of the experiments in cultivation is, that the citrate-soluble phosphoric acid in the bicalcic phosphate proves to possess the same fertilizing value as the water-soluble phosphoric acid in the superphosphate, and consequently the same value as a trade product. That result might, indeed, have been foreseen, inasmuch as it is probable that the superphosphate in the soil is rapidly transformed into bicalcic phosphate through the agency of the compounds of lime present there. This result is supported by the trials carried out by practical agriculturalists, who are well satisfied with both the result of the phosphate and its qualities in general. Owing to its high percentage the freight-charges are low for the valuable ingredient, and a very small amount need be manipulated by the farmer. It is in all other respects easy to handle and does not damage the sacks in the least.

VIII. THE SUPERIOR ADVANTAGES OF THE ELECTROLYTIC METHOD

The merits of the electrolytic method are as follows:—

- a) It admits of the use of cheap low-percentage raw phosphate, not available for the superphosphate industry.
- b) By it, a phosphate containing 35-38% of soluble phosphoric acid is obtained, even from low-percentage raw material.
- c) Freightage for a given quantity of phosphoric acid in the finished article is only about half that in the case of ordinary superphosphate.

- d) Retrogradation of soluble phosphoric acid when stored does not occur.
- e) The raw phosphate need not be reduced to a finely powdered state.
- f) Bicalcic phosphate can be employed as a fertilizer on all kinds of soil, even on sandy and boggy land.
- g) Bicalcic phosphate will be of excellent use in the manufacture of "complete fertilizers."
- h) Sacks are in no wise damaged by the product.
- i) The product is a finely divided, white powder, which is easily spread on the field.

The process is now being carried out in a small factory, the first factory, belonging to the Difosfat Company, Trollhättan, Sweden.

THE ELECTROCHEMICAL BEHAVIOR OF VERY CONCENTRATED THALLIUM AMALGAMS

THEODORE W. RICHARDS AND F. DANIELS

In continuation of previous work on this subject by one of the authors and Dr. J. H. Wilson, the electromotive forces between liquid amalgams of thallium of great concentration were carefully studied at various temperatures. From the temperature coefficients of these concentration cells the heats of dilution were calculated. It was found in every case that the observed electromotive forces greatly exceed those calculated from the concentrations alone. Thus for example in the case of a cell made from amalgams of 3.736 and 21.722% respectively, an E.M.F. of 0.076314 volt was observed, while the concentration effect would be only 0.045292 volt. If to the concentration effect (theoretical) is added the E.M.F. calculated from the heat of dilution, according to the equation of Cady ($\pi = \frac{Q}{nF} + \frac{RT}{nF} \ln \frac{C_1}{C_2}$) the agreement is much better. Thus the quantity $\frac{Q}{nF}$ in the case cited above was 0.04043, and the sum is 0.08572. This *excess* of the sum over the observed value 0.07631 may perhaps be ascribed to partial *association* of the atoms of Thallium in concentrated amalgams.

THE INFLUENCE OF CINDERS ON THE CORROSION OF IRON IMBEDDED IN CLAY

WALTER B. SCHULTE

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Investigations of electrolytic corrosion of underground structures occasionally reveal examples of marked corrosion under certain conditions which preclude a consideration of stray currents from electric railways as the cause. Filled ground seems to be especially harmful to iron pipes, especially where the filling is composed largely of cinders, coal, and furnace products.

Of the various explanations which have been offered to account for this corrosion the more common are that the sulphur, which is a constituent of most coals, probably forms sulphuric acid, with the resultant chemical corrosion; also that cinders and particles of conductive carbon in contact with iron produce a local couple and the pits which are formed are attributed to this effect.

The objection to the former theory is that after a severe heat treatment the sulphur is usually expelled from the cinder material, and that the latter explanation is not completely adequate is indicated by the fact that the corrosion occurs even where there may be an intermediate layer of clay between the cinder bed and the pipe. Certain cases of deep pitting of iron pipe have been called to the attention of the writer where an overlying bed of cinder filling out of direct contact with the pipe seemed to be in a measure responsible for the damage noted.

It is well known that if a mass of carbon and a mass of iron are imbedded in an electrolytic conductor, such as in moist earth, a difference of potential is established between these two bodies, the iron being electrochemically positive to the carbon. This potential does not establish a flow of current unless metallic contact is made between these two bodies. While a layer of carbon material may be separated from an iron pipe in one local-

ity by a bed of sand or clay, corrosion may be produced at that locality by reason of contact between the iron and the carbon bed at some other position, such for example as occurs where a service pipe or other portion of the underground system may pass through the carbon bed. It is evident therefore that contact between the cinders and the iron is not necessary at the exact location where the corrosion is observed in order to account for such corrosion.

An active couple produced by carbon and iron results in the iron being the anode and the carbon being the cathode. Polarization tends to reduce the flow of current but this polarization is minimized if air has ready access to the carbon bed; therefore the nearness of the carbon bed to the surface of the earth is a factor which influences the corrosion caused by such material.

The object of the investigation here described was to reproduce in the laboratory conditions which were found in the field and to make laboratory measurements of potential and current flow, and determination of the amount of corrosion. The experiments were carried out in the Chemical Engineering Laboratories of the University of Wisconsin.

APPARATUS

The apparatus, as set up in the laboratory, included a sheet of iron buried in a bed of clay on the top of which rested a layer of granular graphite which represented the cinder bed. Electrical contact between the plate and cinders was provided for by a wire connected between them. The arrangement of the apparatus is shown in Fig. 1.

It is of course evident that the conductive layer of carbon here used has a higher electrical conductivity than that produced by cinder filling, as found in practice, and the reason for using this was to accelerate the action so as to produce measurable results within a short time.

The iron plate was of No. 24 sheet iron which was pickled, dried and weighed before being placed in the clay which was taken from a fresh excavation and was moist when placed in the

box. The layers below and above the plate were well tamped in place. The carbon, which had been used as a resistor in electric furnaces, was granular, the particles ranging from $\frac{1}{4}$ " to $\frac{1}{2}$ " in diameter. A graphite block, with a steam, was placed in the carbon to make electrical contact between the carbon and external connections, and insulated wire connected to the plate was brought out through the clay. The carbon lead was connected to a switch also connected to the iron plate terminal so that by

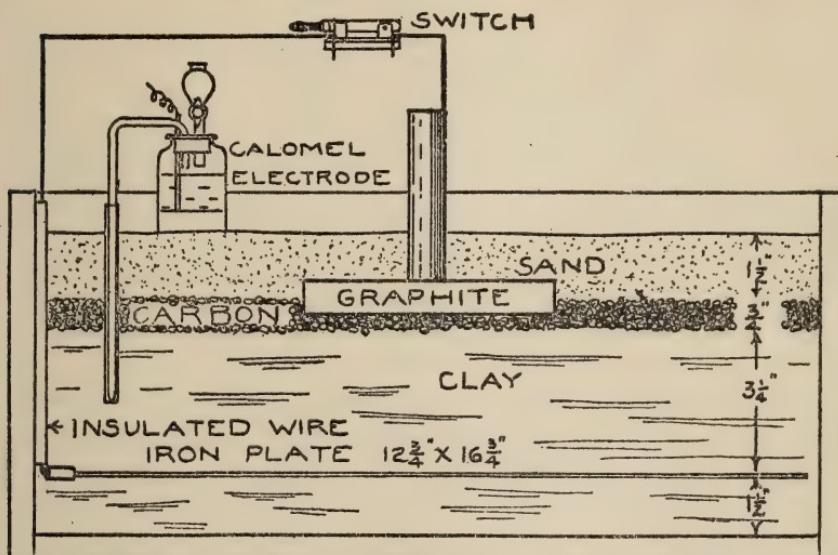


FIG. 1.

closing it the cell was short circuited. The switch was provided with short leads so that an ammeter or voltmeter could be connected to them and measurements be made with the switch open. The carbon was covered by a $\frac{1}{2}$ " layer of sand at the beginning of the test but this was removed on the fourth day.

To measure the single potentials of the iron and carbon against the clay a calomel electrode was employed with a long nose reaching down through a glass tube into the clay half way between the carbon and iron. A few drops of normal KCl were poured into the bottom of the glass tube to moisten the clay and assure good contact between the clay and electrode.

MEASUREMENTS

Before closing the switch, the potentials of the iron and carbon against the clay were determined by the potentiometer method taking -0.56 volt as the potential of the calomel electrode. The results are given below;—

| | |
|----------------|-----------------------------|
| Total E. M. F. | 0.842 volts, carbon cathode |
| Clay to carbon | -0.638 volts |
| Iron to clay | +0.204 volts |
| <hr/> | |
| Total | 0.842 volts |

A voltmeter indicated 0.83 volts.

After making the single potential measurements the circuit was inadvertently closed for a minute or two after which the voltage, as indicated by a voltmeter, had fallen to .72 volts. Further short circuiting caused the voltage to drop from .68 to between .45 and .50 after a few minutes. One and one-half minutes after opening the switch the voltage increased to .68 volts.

The cell was short circuited for twenty minutes and the switch then opened, after which single potential measurements were made at various intervals.

After being on short circuit for seventeen hours, similar single potential measurements were made, during which time the average current, as measured by a milliammeter was .0515 amperes. The data of these measurements as tabulated in Table I and plotted in Fig. 2 show that the rate of depolarization is decreased after the cell has been short circuited for the longer time.

The cell was then allowed to stand short circuited and readings were made of the voltage and current at various times and during the run the results of which are tabulated in Table II. The instruments were of standard make and in good calibration and of the following scales and resistances;—

Voltmeter 0-15 volts; 53.5 ohms resistance
Ammeter 0-500 mil-amperes; 0.09 " "

During the fourth day the layer of sand above the carbon was

TABLE I
Depolarization

| Single Potentials of Carbon | | | | Single Potentials of Iron | | | |
|-------------------------------|-------|-----------------------------|-------|-------------------------------|----------|-----------------------------|----------|
| Short circuited 20 minutes | | Short circuited 17 hours | | Short circuited 20 minutes | | Short circuited 17 hours | |
| Time | Time | Time | Time | Min. | E. M. F. | Min. | E. M. F. |
| 1/2 | -.432 | 0 | -.394 | 0 | +.184 | 0 | +.162 |
| 1 | -.478 | 1 | -.424 | 1/4 | +.184 | 1 | +.160 |
| 2 | -.485 | 1-1/2 | -.434 | 3/4 | +.186 | 2 | +.160 |
| 3 | -.508 | 2 | -.438 | 2 | +.180 | 3 | +.160 |
| 4 | -.510 | 3 | -.442 | 3 | +.182 | 4 | +.160 |
| 5 | -.516 | 4 | -.452 | 4 | +.180 | 5 | +.160 |
| 7 | -.524 | 5 | -.452 | 6 | +.178 | 8 | +.158 |
| 10 | -.530 | 8 | -.458 | 24 | +.180 | 10 | +.158 |
| 24 | -.540 | 10 | -.468 | | | 16 | +.158 |
| 42 | -.564 | 16 | -.470 | | | 23 | +.156 |
| | | 23 | -.474 | | | 43 | +.156 |
| | | 43 | -.484 | | | 60 | +.158 |
| | | 60 | -.499 | | | | |

removed as noted in the table. The clay began to dry out, so that beginning with the tenth day about half a liter of water was sprinkled over the carbon and allowed to soak in before a set of readings were made. No readings were taken between the 33rd and 58th days, nor was the cell moistened, with the result that the current on the 58th day was almost nil, and the potential .22 volt. Three minutes after the cell had been moistened the observed values increased to .0175 amperes and .32 volt.

Rough integration of the curve plotted between current and days, with the current as zero on the 58th day, gives 35 amperes hours. If the cell had been moistened regularly each day throughout the test it is fair to assume that the average current would have been .03 ampere. .03 ampere for 58 days is equivalent to about 42 ampere hours. The average voltage over this period can be taken as .35 volt.

The interesting point to be noted is that as long as the clay was moist a current flowed continuously from the iron to the

carbon, the depolarization due, presumably, to the action of the air on the carbon, taking place at a constant rate.

The loss of iron by one ampere-year is about 20 pounds so that .03 ampere, the assumed average current with the clay moist, would be about $20 \times .03 = .6$ pound.

The area of the plate was 1.45 square feet or 2.9 feet total surface, so that the theoretical corrosion per square foot would be

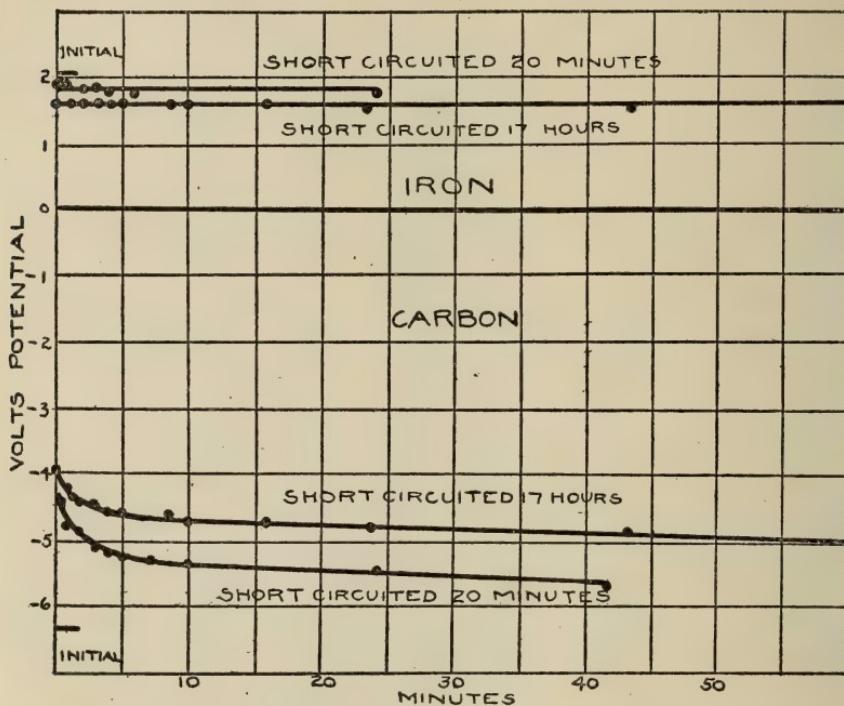


FIG. 2.

.23 pound per year or about $\frac{1}{4}$ pound per year. The loss of $\frac{1}{4}$ pound per foot from each surface of a plate would destroy the equivalent of a No. 30 sheet in one year or half of a No. 24 sheet. If this corrosion were concentrated in six square inches area on every square foot, the metal would be pitted to the depth of .15 inch which would pierce a three inch cast iron main in a little over two and one-half years.

TABLE II
Current and Voltage Readings

| Day | Amperes | Volts | Remarks |
|-----|---------|-------|------------------------|
| 1 | .052 | .45 | |
| 2 | .0518 | .50 | |
| 3 | .050 | .45 | |
| 4 | .051 | .45 | Sand removed from top. |
| 5 | .051 | .44 | |
| 7 | .0495 | .38 | |
| 8 | .035 | .40 | |
| 9 | .030 | .20 | |
| 10 | .040 | | Began wetting. |
| 11 | .035 | .40 | |
| 12 | .0475 | .42 | |
| 14 | .0475 | .42 | |
| 15 | .040 | .42 | |
| 17 | .041 | .40 | |
| 24 | .030 | .35 | Dried out since last |
| 25 | .0375 | .36 | reading. |
| 29 | .023 | .30 | |
| 30 | .020 | .20 | |
| 31 | .035 | .40 | |
| 32 | .028 | .35 | |
| 33 | .028 | .35 | |
| 58 | .015 | .32 | |

CORROSION OF PLATE

After the 58th day the cell was dismantled. Examination of of the clay near the plate showed that the rust had penetrated into it as much as $\frac{1}{4}$ " in some places. The plate was spotted with oxide and greenish iron compounds. Corrosion was noticed both on the upper and lower sides of the plate and the corner diagonally opposite the wire connection was eaten through.

The plate was washed, the greater part of the rust scraped off and the remainder then dissolved off by hot ammonium citrate, after which it was weighed. The data follow:—

| | |
|----------------------------------|-------------|
| Weight of plate before test..... | 401.6 grams |
| Weight of plate after test..... | 346.5 grams |
| Loss..... | 55.1 grams |

Thirty-five ampere hours theoretically would corrode 36.4 grams of iron so that the efficiency of corrosion in this case would be 55.1 or about 150 per cent. That is, it may be said that two-thirds of the loss by corrosion was due to the current produced by the difference of potential between the carbon and the iron.

These experiments were intended as preliminary work for further investigation, which, however, was not undertaken, but a description of this first, rather incomplete work, it was thought, would prove of interest and draw attention to the influence of carbon and cinders on the corrosion of iron and perhaps lead to further experimentation on the subject. Further work along this line should be undertaken with the conditions more closely approaching those actually found; that is, using cinders instead of carbon and putting them, with the iron plate, in the earth. Similar plates not connected with the carbon should also be buried so that the amount of natural corrosion can be determined. Under these conditions, with the higher resistant cinders, it is to be expected that less current would be produced.

An interesting case of corrosion of a gas pipe which may be explained by action similar to that discussed above has been observed recently by the writer. Along a certain street the gas mains were paralleled by a water main buried a short distance beneath. The soil is mainly clay or silt but at the lowest portion of the street the water main dipped into a peaty layer. The gas main lay in the clay above the peat at this point and was corroded through at several places. The main apparently was in a locality not subjected to stray currents from the street railway or grounded power circuits so that the currents causing the corrosion must have come from other sources.

A length of gas main about 400 feet long was disconnected from the adjoining portion. Potential measurements between this disconnected length and an iron rod driven in the black layer showed that the gas main was .3 volt positive, and readings

between gas and water connections showed that current was flowing from the gas to the water main through the earth. The corrosion can be explained by the fact that peat sets up a different potential toward an iron surface than does clay, and connections between the gas and water services on the consumer's premises makes the couple electrolytically active thereby producing electrolytic corrosion.

(Summary)

STUDIES ON THE SILVER COULOMETER

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1. It was found that the slightest traces of impurities such as dust and organic matter effected a silver nitrate solution so that it gave abnormally heavy deposits. Particular attention was paid to preparing a reproduceable "normal electrolyte." It was necessary to take unusual precaution in preparing all materials and we used only quartz, gold and platinum utensils.

2. In preparing atomic weight silver the usual method was modified, we found the conditions under which silver could be precipitated, from an ammonical solution of silver chloride, in a crystalline condition and this is a distinct advantage over reducing solid silver chloride with sugar and KOH.

3. In preparing pure water particular attention was paid to the exclusion of dust and organic matter of all kinds, even to the burning of volatile organic matter which might be present in the air that came in contact with the solutions used. The water came in contact only with quartz since the solubility of glass sufficed to measurably effect a silver nitrate solution.

4. Silver nitrate was obtained from atomic weight silver and pure nitric acid, the excess of acid being driven off at a definite temperature in an electric furnace and with the exclusion of organic matter, there was formed a solution which contained equal equivalents of Ag. & No₃ Kahlbaum's C. P. silver nitrate recrystallized and fused gave a deposit 0.009% heavier than our normal electrolyte and other solutions distinctly heavier deposits.

5. Four porous cup coulometers were run in series, the cathode cups in 1 and 2 were of platinum while 3 and 4 were gold. They contained the same solutions and were treated in exactly the

same manner. In every case we found the deposits on gold to be heavier than on platinum, the average excess was 12 parts in 100000.

6. In experiments where a Rayleigh form which contained Kahlbaum's C. P. silver nitrate solution was run in series with our normal coulometer, the Rayleigh gave a deposit 0.036% too heavy. The anode of the coulometer was wrapped in filter paper and the anolyte diffused through to the cathode during electrolysis.

7. In our porous cup coulometers the anolyte was always lower than the catholyte and the anolyte did not flow through except in special experiments which show that when the anolyte is allowed to pass through the porous cup and come into contact with the cathode, a heavier deposit was obtained by 0.019%. This is nearly one-half of the abnormal effect caused by the heavy anode liquid and filter paper as shown in the Rayleigh form.

Experiments were made with thin walled porous "Alundum" cups as a substitute for the porcelain cups. The silver deposited while using these alundum cups was abnormally heavy, a result which may be unquestionably attributed to the anolyte diffusing through the porous cups and coming into contact with the cathode during the electrolysis.

(*Abstract*)

THE VAPORIZATION OF METALLIC CATHODES IN THE GLOW DISCHARGE

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In order to investigate the conditions that are essential to the existence of an electric arc, a series of experiments was carried out, in which the metallic cathode in a glow discharge was allowed to become heated by gradually increasing the current, until the change to an arc took place. The cathode consisted of a globule of metal from 6 to 12 mm. in diameter, resting in a shallow cavity on a plate of fused silica or alundum. Electric contact was made by means of a short rod of tungsten which extended through a hole in the plate. The lower end of this rod was inserted in a carbon post in order that the heat generated at the cathode by the glow discharge might be carried away as slowly as possible. The anode was in most cases a rod of tungsten. With not more than a few tenths of an ampere flowing, the temperature of the cathode rose in a few moments above the melting point. As the current was further increased, lively vaporization set in, and the boiling point of the metal was approached, if not actually reached, before the glow changed to an arc. In the case of Ag, Cu, and Fe, this took place at a white heat. With Bi, Hg, and Cd, incandescence was of course impossible.

Observations were made in nitrogen and hydrogen at various pressures. The arc came at a higher temperature and larger current the higher the gas pressure. Trouble was experienced from the formation of impurities on the surface of the cathode, especially in the case of the more easily oxidizable metals. But even when considerable slag was present, the negative glow usually drove it back as soon as the metal melted, allowing the

discharge to take place from clean metal, until with increasing current the mantle had grown to such an extent that it heated the slag and thus produced an arc. The formation of an arc was greatly accelerated in the presence of traces of oxygen. In many cases, the liberation of occluded gas was noted as the globule was heated, but this seemed to be without influence on the transition to an arc. When the cadmium cathode was used, a thermo-element was imbedded in it to determine the relative changes in temperature.

For the present, we must select as the definition of an electric arc one that is non-committal as to the part played by incandescence and vaporization of the cathode metal. The present investigation shows that these are quite insufficient of themselves to cause an arc to form, and indicates that either the attainment of the boiling point of the cathode, or the presence of impurities, is an essential condition.

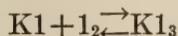
(*Abstract*)

ABSORPTION SPECTRA OF SOLUTIONS OF SOME PERIODIDES

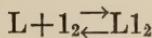
FREDERICK H. GETMAN
Stamford, Conn.

Absorption spectra of solutions of iodine in sodium iodide, potassium iodide, rubidium iodide and potassium bromide have been photographed in the visible region of the spectrum and the spectrograms so obtained have been compared with spectrograms of brown solutions of iodine in non-aqueous solvents.

The absorption spectra of the periodide solutions are found to be similar to the absorption spectra of the brown non-aqueous solutions. Since in the periodide solutions we have the equilibrium



A similar equilibrium



(Where L denotes the solvent) is suggested as obtaining in brown non-aqueous solutions of iodine. This is in accord with the views of other investigators.

UEBER REZIPROKE SALZPAARE UND DOPPELT- TERNÄRE SALZMISCHUNGEN

PROF. DR. ERNST JÄNECKE

Hannover, Germany

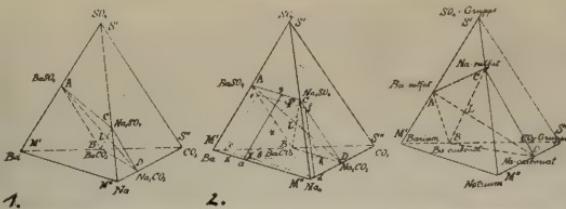
EINLEITUNG

Im folgenden sollen vom Standpunkt der Phasenlehre aus die heterogenen Gleichgewichte fest-flüssig der reziproke Salzpaare und der Mischungen behandelt werden, die ich als doppelt-ternäre Salzmischungen bezeichnen möchte. Eine derartige Darstellung dürfte besonders auch in dem Vaterlande von William Gibbs Interesse finden. Diese Salzmischungen stellen ein weites bisher stark vernachlässigtes Arbeitsfeld dar, obwohl sie nicht nur erhebliches theoretisches, sondern auch vielfach praktisches Interesse besitzen. Der Grund hierfür liegt zum Teil darin, dass man sich bei der Untersuchung von Lösungen zu lange einseitig mit verdünnten Lösungen beschäftigt hat, während solche mit festen Bodenkörpern natürlich meistens konzentriert sind. Bei den verdünnten Lösungen spielt der anschauliche Begriff des osmotischen Druckes eine grosse Rolle, während bei der Untersuchung konzentrierter Mischungen andere Größen z. B. die freie Energie oder am besten das thermodynamische Potential benutzt werden müssen. In folgendem ist daher zur Auseinandersetzung des Gleichgewichtes das thermodynamische Potential verwendet. Dass man viele Resultate bei Mehrstoffmischungen auch ohne Benutzung des thermodynamischen Potentials, einfach mit der Phasengleichung finden kann, habe ich z. B. bei den Untersuchungen über isomorphe ternäre Mischungen mit Mischungsstücken in festen und flüssigem Zustande (Zeitschrift für physikalische Chemie 67, 1909, 641–668) und bei den von mir bisher veröffentlichten Untersuchungen über reziproke Salzpaare gezeigt (Zeitschrift für physikalische Chemie 64, 1908, 305–327).

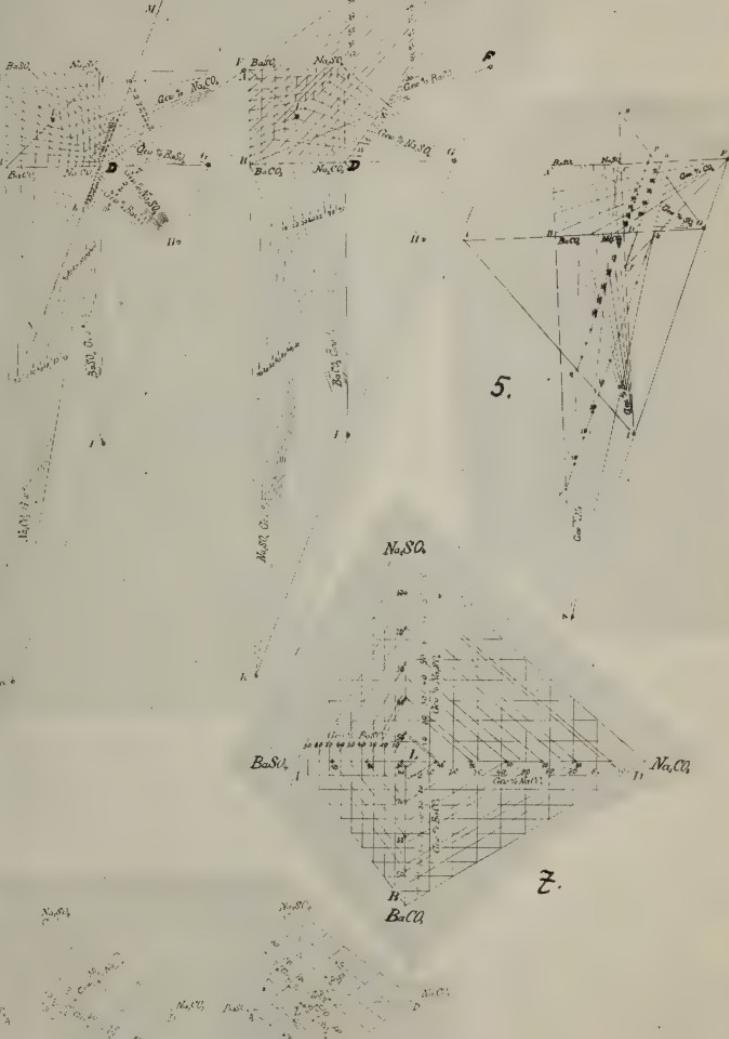
Erst dann wenn man die Werte des thermodynamischen Poten-

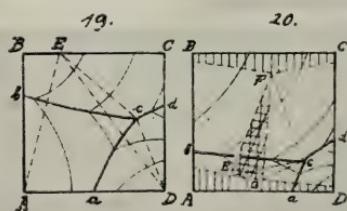
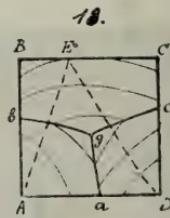
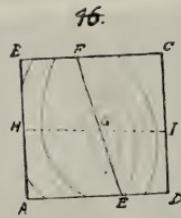
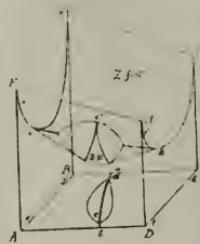
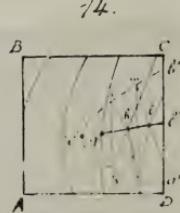
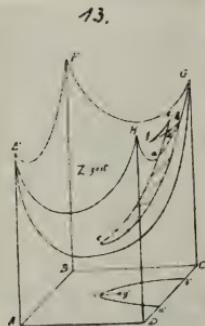
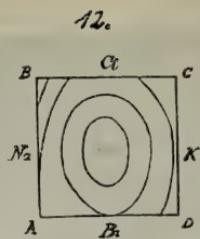
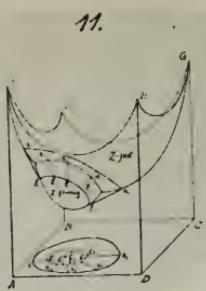
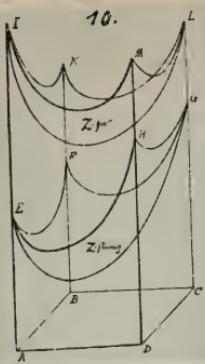
tials wirklich berechnen kann, ist die Theorie vollkommen. Die Anfänge hierfür sind durch die erweiterte Theorie von van der Waals gemacht und besonders von van Laur weiter ausgebildet. Die Theorie beschränkt sich aber bis jetzt im wesentlichen auf Zweistoffmischungen. Solange aber keine Zustandsgleichungen für Mehrstoffmischungen benutzt werden können, oder benutzt werden, ist man auf Annahmen über die Werte des thermodynamischen Potentials in Beziehungen zu Temperatur, Druck und Konzentration angewiesen und hierin liegt die Gefahr, Fälle zu konstruieren, die in Wirklichkeit nie eintreten werden. Am bekanntesten in dieser Hinsicht ist der Typus von binären Mischkrystallen, dem man ein Schmelzpunktmaximum zuschreibt. Dieser Typus, der sich bei bestimmten Annahmen der Beziehungen des thermodynamischen Potentials für binäre Flüssigkeitsmischungen und für feste isomorphe Mischungen leicht ableiten lässt, tritt trotzdem nicht auf, weil er sich mit den Folgerungen aus der Theorie von van der Waals über die Zustandsgleichung binärer Mischungen nicht vereinigen lässt. Da denn auch noch nie der Fall eines Schmelzpunkts-Maximum bei Isomorphie gefunden wurde, während bis jetzt bereits über 60 Fälle eines Minimum und über 20 Fälle ohne Minimum oder Maximum gefunden sind, so ist dieses umgekehrt auch ein Wahrscheinlichkeitsbeweis für die Richtigkeit der benutzten Theorie. Es zeigt sich also dass sogar verhältnismässig einfache Annahmen über die Veränderlichkeit des thermodynamischen Potentials falsch sein können. Mir erscheinen in dieser Hinsicht auch verschiedene neuere Untersuchungen bedenklich, wo ohne weitere Grundlage Annahmen über das thermodynamische Potential gemacht sind. Bekanntlich liegt das wertvolle beim thermodynamischen Potential vor Allem in seiner einfachen Beziehung zu Druck und Temperatur, wovon auch weiter unten ausführlich die Rede ist.

Da es sich bei heterogenen Gleichgewichten um Phasen verschiedener Zusammensetzung handelt, habe ich zunächst eine Darstellung der Mischungsverhältnisse in Molekülprozente bei reziproken Salzpaaren gegeben und ihre Beziehung zu Gewichtsprozenten graphisch dargestellt. Diese Darstellung habe ich zum Teil schon kürzlich auseinandergesetzt. (Zeitschr. f. anorg. Chem. 71, 1911, 1-18).

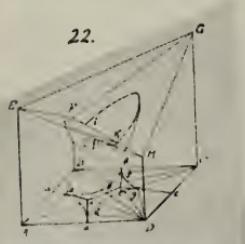
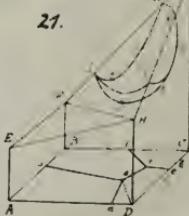


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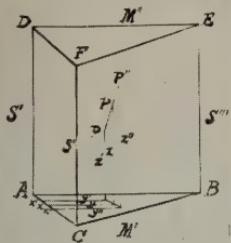


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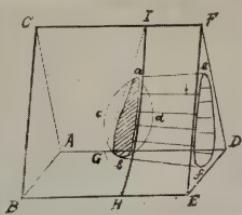


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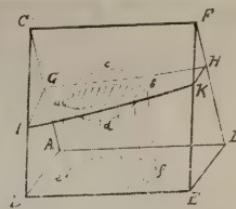
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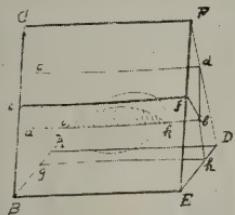
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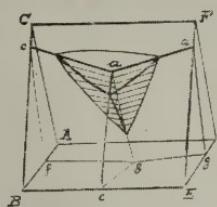
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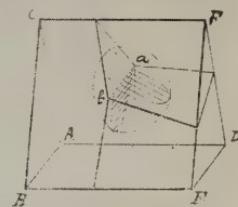
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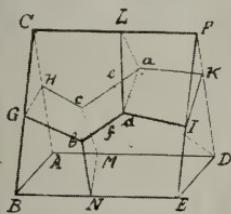
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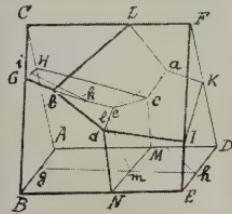
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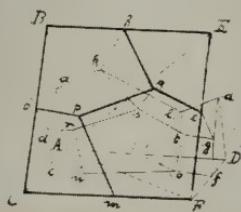
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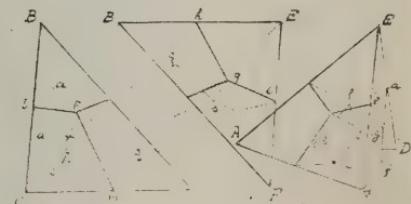
31.



32.



33.



Vollständig neu ist aber eine ebene Darstellung der Mischungen reziproker Salzpaare, die sich direkt auf Gewichtsprozente bezieht. Weiterhin ist das Verhalten von Salzmischungen der angegebenen Art für das Gleichgewicht fest-flüssig untersucht, indem die Zahl des auftretenden Bodenkörpers als Einteilungsgrund gewählt wurde. Eine vollständig erschöpfende Darstellung ist bei der Fülle des Stoffes unmöglich. Es ist daher besonders Wert darauf gelegt, Beispiele heranzuziehen, die bei den einzelnen Fällen wahrscheinlich sind.

Hieran schliesst sich eine kurze Behandlung der doppelt-ternären Salzmischungen, die naturgemäß wegen der noch grösseren Kompliziertheit der Systeme noch weniger vollständig ist.

Ich würde es besonders begrüssen, wenn hierdurch neue Experimentaluntersuchungen angeregt würden.

Allegemeines. In der Chemie hat man sehr häufig Untersuchungen in der Ausscheidung einer festen Verbindung, die allgemein durch eine Gleichung: $M'_mS'_n + M''_oS''_p = M'_mS''_p + M''_oS'_n$ ausgedrückt werden können. Hierfür sind M' und M'' Metalle (oder auch NH_4 , Wasserstoff und dergl.) und S' und S'' Säurereste (oder auch Sauerstoff, Schwefel und dergl.) während m n o p ganze Zahlen sind. Obige Gleichung umfasst z. B. sämtliche Fällungsreaktion der analytischen Chemie. Sind die vier Stoffe die an der Reaktion teilnehmenden Salze so spricht man von reziproken Salzpaaren. Fällt bei einer Reaktion ein fester Körper aus, so hat man natürlich ein Gleichgewicht zwischen fest-flüssig. Der Niederschlag (Bodenkörper) befindet sich im Gleichgewicht mit der übrig bleibenden Flüssigkeit. Es kann auch vorkommen, dass gleichzeitig zwei Bodenkörper zur Ausscheidung kommen wie bei der Reaktion: $BaS + ZnSO_4 = ZnS + BaSO_4$.

Die Gesetze die derartige Gleichgewichte beherrschen, sind auf die Phasenlehre begründet. Bilden sich gallertartige Niederschläge, so ist die Phasenregel nicht ohne weiteres anwendbar solche Reaktionen sollen deshalb hier keine Berücksichtigung finden.

Es handelt sich also um die Gleichgewichte fest-flüssig, bei denen die Bodenkörper krystallinisch sind. Hierbei soll die obige Gleichung der reziproken Salzpaare auch benutzt werden, wenn es sich um Wasserstoff—(also $M' = H$) oder Sauerstoffverbin-

dungen (also $S' = O$) handelt, ja auch wenn gleichzeitig $M = H$ und $S = O$ ($n = 1$ $m = 2$) also Wasser H_2O in der Gleichung enthalten ist. Damit fällt auch ein Teil der wässerigen Lösungen in die folgende Behandlung, während sonst nur Salzmischungen als solche behandelt werden.

Es kann ferner auch vorkommen, dass $M'_m S'_n$ einfach zu einem Metall wird, wie in der Gleichung $Pb + KNO_3 = PbO + KNO_2$.

Man erkennt, dass die Gleichgewichte fest-flüssig bei reziproken Salzpaaren ein hervorragendes Interesse besitzen. Die bisher ausgeführten Untersuchungen sind meistens in wässriger Lösung gemacht, was besonders zweierlei Unterschiede gegenüber den Gleichgewichten im Schmelzfluss bedingt. Einmal untersucht man bei wässerigen Lösungen die Gleichgewichte bei verhältnismässig niedrigen Temperaturen. Erhält man hierbei Ausscheidungen fester Körper, also ein Gleichgewicht fest-flüssig, so kann dieses bei höherer Temperatur ganz anders sein. Die Bodenkörper derselben Mischungen können mit der Temperatur sehr wechseln. Vor allem treten aber bei höherer Temperatur auch häufig Mischkristalle auf (z. B. bei $KCl - KBr$), die bei niedriger Temperatur nicht beständig sind. Es kann dann die obige Gleichung der Zusammengehörigkeit der verschiedenen Salze überhaupt jeder Sinn in Bezug auf das Gleichgewicht fest-flüssig verlieren, indem die feste Ausscheidung gar nicht durch eine einfache Formel ausgedrückt werden kann.

Die anderen Unterschiede in den reziproken Salzpaaren können in der Einwirkung des Wassers liegen. So ist z.B. die Fällung von Chlorsilber aus den Lösungen von Chloriden mittels Silbernitrat, die man durch eine Gleichung $KCl + AgNO_3 = AgCl + KNO_3$ ausdrücken kann, bekanntlich richtiger zu schreiben.

$$\begin{array}{c} + \\ Ag \\ + \end{array} + \begin{array}{c} - \\ Cl \\ - \end{array} = \begin{array}{c} + \\ AgCl \\ + \end{array} + \begin{array}{c} (-) \\ (+) \\ (-) \end{array}$$

Die beiden Salze sind durch die Auflösung in Wasser teilweise elektrolytisch dissociert und die Fällung ist auf die Neutralisation der verschiedenen elektrisch geladenen Ionen zurückzuführen.

Bei den folgenden Untersuchungen über die Gleichgewichte zwischen fest-flüssig bei reziproken Salzpaaren im angegebenen erweiterten Sinne ist angenommen, dass die Verbindungen $M'_m S'_n$, $M''_o S''_p$, $M'_m S''_p$, $M''_o S'_n$ stets entweder in Mischung mit einander oder als solche in den Gleichgewichten auftreten, dass

also niemals die freien Elemente (oder Radikale) M' , M'' , S' , S'' oder gar deren Zersetzungspprodukte (z. B. bei SO_4) in Frage kommen. Durch diese Einschränkung werden die Mischungen reziproker Salzpaare zu einen Dreistoffsysteme, woraus folgt, dass ihre Mischungsverhältnisse sich durch eine ebene Darstellung zum Ausdruck bringen lassen müssen. Allerdings werden sie zu einem Dreistoffsystem besonderer Art, indem man nicht drei beliebige der vier Salze als unabhängige Bestandteile wählen darf. Dieses bedingt besonders interessante Unterschiede gegenüber den gewöhnlichen Dreistoffmischungen, deren Gesetze beim Schmelzen und Erstarren im wesentlichen bekannt sind (vergl. besonders das dritte Heft von Roohebooms Phasenlehre von Schreinemakers, sowie die grosse Anzahl Abhandlungen in der Zeitschrift für physikalische Chemie und den verschiedenen holländischen Zeitschriften).

DIE GRAPHISCHE DARSTELLUNG DER MISCHUNGEN REZIPIROKER SALZPAARE

Die Darstellung soll an Mischungen der Salze, die in der Gleichung $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$ vorkommen auseinander gesetzt werden. Um zu ebenen Darstellungen zu kommen, muss man zunächst die Mischungen von 4 einander ganz fernstehenden Stoffen betrachten. Diese werden bekanntlich am besten durch ein reguläres Dreieck dargestellt. In der ersten Figur sind M' , M'' , S' , S'' die Eckpunkte des Tetraäders und in der zweiten: M' , M'' , S' , S'' . Rechnet man mit Molekülprozenten, so liegen die Verbindungen $M'S'$ ($BaSO_4$), $M''S''$ ($BaCO_3$), $M'S''$ (Na_2CO_3) und $M''S'$ (Na_2SO_4) in den Punkten A, B, C und D. Das Viereck A B C D ist ein ebenes Viereck und zwar in Figur 2 ein Quadrat.

Für die unten angegebenen Gleichgewichte soll immer ein Quadrat bemerkt werden. Es sind dann in den Endpunkten des Tetraäders die Molekularwerte für M'_m , S'_n , M''_o , S''_p anzunehmen wodurch die Verbindungen $M'_mS'_n$, $M''_oS''_p$, $M'_mS''_p$, $M''_oS'_n$ in die Halbierungspunkte der Tetraäderseiten zu liegen kommen. Hat man nun einen beliebigen Punkt P (Figur 2) im Quadrate, so stellt derselbe ein Mischungsverhältnis dar von der

Formel $\text{Na}_{2x}\text{Cl}_{2y}(\text{SO}_4)_2\text{Ba}_{1-x-y-z}$ (allgemein $M''_{ox}S''_{py}S'_{mz}M'_{n(1-x-y-z)}$) wobei x, y und z die Koordinaten parallel den drei aus M' auslaufenden Tetraäderkanten sind und die Tetraederseite gleich Eins ist. Da die Mischung neutrale Salze zur Darstellung bringt, muss $y + z = x + (1 - x - y - z) = 1 - (y + z)$ sein, also $y + z = \frac{1}{2}$. Dieses folgt auch aus der Figur 2. Man kann daher eine (y) der drei Variablen eliminieren und hat dann das Mischungsverhältnis $\text{Na}_{2x}\text{Cl}_{2(\frac{1}{2}-z)}(\text{SO}_4)_z\text{Ba}_{(1-x)}$. Hierbei liegen die Werte von x und z zwischen 0 und $\frac{1}{2}$. Setzt man $2x = x'$ und $2z = z'$ so erhält man für alle Mischungen die Formel $\text{Na}_{2x'}\text{Cl}_{2(1-z')}(\text{SO}_4)_z\text{Ba}_{(1-x')}$ indem x' und y' zwischen 0 und 1 variieren. Durch die beiden Diagonalen wird das Quadrat in zwei Paare gleichschenklig-rechtwinklige Dreiecke zerlegt, diese drei der vier Salze in den Endpunkten enthalten. Für jede Mischung lässt sich durch Parallelen zu den Quadratseiten und den Diagonalen und Abmessung der Abschnitte das Molekülverhältnis der drei zugehörigen Salze auf doppelte Art berechnen.

Diese Darstellung der Mischungsverhältnisse im Quadrat bezogen auf chemische Formeln lässt sich durch Scharen von Geraden überdecken, die sich direkt auf Gewichtsprozente beziehen (vergl. Jänecke Ztschr. für anorg. Chemie 71, 1911, 1–18 und Metallurgie 1912 Heft 10 und Hofmann Metallurgie 1912, 133–140).

Verlängert man die Quadratseiten und die Diagonale nach den Richtungen der Salze mit geringerem Molekulargewicht hieraus um die Länge $l \frac{m_r}{m_p - m_r}$ wenn m_r das Molekulargewicht des leichteren, m_p des schwereren Salzes und l die Länge der Seite, oder bei Verlängerung der Diagonalen der Diagonale ist, so erhält man 6 Punkte E, F, G, H, J, K die in einer Geraden liegen. Von diesen Punkten aus kann man durch Scharen von Geraden wie dieses die Figuren 3 und 4 angeben die Gewichtsprozente zum Ausdruck zu bringen. Bei Figur 3 ist das Quadrat durch die Diagonale AD ($\text{BaSO}_4 - \text{Na}_2\text{CO}_3$) und bei Figur 4 durch BC ($\text{BaCO}_3 - \text{Na}_2\text{SO}_4$) in zwei Dreiecke zerlegt. Die Art wie von 10 zu 10 Prozent zum Beispiel aus dem Punkte H die Geraden zu ziehen sind, zeigt Figur 3. Eine Parallelle MN zu E, F, G, H, J, K durch D schneidet die Geraden BH und CH in den

Punkten b und c. Teilt man Db in 10 gleiche Teile und ebenso Dc so geben die Geraden aus H durch diese Teilpunkte 1, 2, 3, 4, 5, 6, 7, 8, 9 und I, II, III, IV, V, VI, VII, VIII, IX die Gewichtsprozente BaCO und Na₂SO₄ von 10 zu 10 Prozent in den beiden Dreiecken ABD und ACD an. Aehnlich liessen sich für alle Bündel durch solche Parallelen die Gewichtsprozente finden: Es sind immer die Abschnitte der Parallelen durch die Schenkel der Winkel aus E, F, G, H, J, K in zehn Teile zu teilen und die Teilpunkte mit diesen Punkten durch Gerade zu verbinden. Auch die Gewichtsprozente bezogen auf die Salzbestandteile M'M'' S'S'' für sich lassen sich bei Berechnung der Punkte F, G, J, K, konstruieren. In diesem Falle hat man noch die Gerade Ff, Gg, Ii und Kk zu ziehen. Hierbei ist Cg = 1 $\frac{m_d}{m_{s''}}$, Bi = 1 $\frac{m_d}{m_{m''}}$, Dk = 1 $\frac{m_b}{m_{m'}}$ und Df = 1 $\frac{m_o}{m_{m''}}$ wenn m_d, m_b, m_o, m_{s''}, m_{m''}, m_{m'}, und m_{s'} die Molekulargewichte von D (Na₂CO₃), B (BaCO₃), C (Na₂SO₄), S''(CO₃), M''(Na₂), M'(Ba) und S'(SO₄) sind.

Teilt man die durch F, G, J, K gezogenen Parallelen Dp, Dq, fo und kr in zehn gleiche Teile so erhält man durch Verbindung dieser Teilpunkte mit F, G, J, K, direkt die Geraden die im Quadrate die Gewichtsprozente der Salzbestandteile angeben. Diese für das bestimmte Salzpaar gewählte Darstellung lässt sich leicht auf andere übertragen.

Bei Vergleich verschiedener Salzmischungen benutzt man am besten stets die Darstellung im Quadrate, da hierbei auch die Auffindung von Gewichtsverhältnissen nicht sonderlich umständlich ist. Es gibt aber auch eine ebene Darstellung, die sich direkt auf Gewichtsprozente bezieht und die in einigen Punkten noch einfacher ist. Bei bestimmten technischen Betrieben, die sich auf solche Darstellung stützen, würde diese vor der anderen einen Vorzug besitzen.

Dass eine eben Darstellungsform für reziproke Salzpaare unter Benutzung von Gewichtsprozenten möglich sein muss, erkennt man leicht, wenn man auf das Tetraäder zurückgeht und alle Mischungen auf Gewichtsprozente bezieht. Hat man z.B. die vorigen Mischungen, so liegen, wie Figur 6 zeigt, die Salze des reziproken Salzpaars in gewissen Punkten A, B, C, D der vier begrenzenden Tetraäderkanten M'S'', M'S'', M''S' und M''S''.

Die Lage dieser Punkte A, B, C, D ist durch die Zusammensetzung der Salze eindeutig bestimmt und das unregelmässige Viereck A, B, C, D stellt sämtliche Mischungen des reziproken Salzpaars dar. Dieses Viereck könnte man für die Darstellung aller Mischungen benützen. Es lässt sich jedoch aus ihm ein anderes Viereck noch leichter konstruieren. Hierfür denke man sich das Gewichtsverhältnis durch Tetraäder mit beliebigen Kantenlängen und Winkeln ausgedrückt. Jedes ergibt dann ein gewisses Viereck als Darstellung des reziproken Salzpaars. Diese Vierecke haben ein sehr verschiedenes Aussehen. Alle haben aber das gleiche Längenverhältnis $\frac{AL}{DL}$ und $\frac{CL}{BL}$ wenn der Schnittpunkt L der Diagonalen dem Mischungsverhältnis $M'_s M'' S''$ (als Formel angenommen) entspricht. Diese Mischung lässt sich nach den beiden Salzen auf den Diagonalen in $M'_m S'_n + M'_o S'_p$ oder $M'_m S''_o + M''_p S'_n$ zerlegen. Das Längenverhältnis $\frac{AL}{DL}$ ist daher gleich dem Gewichtsverhältnis $\frac{M'_o S'_p}{M'_m S'_n}$ und das Längenverhältnis $\frac{CL}{BL}$ gleich dem Gewichtsverhältnis $\frac{M'_m S'_p}{M'_o S'_n}$. Von den Vierecken, die sich aus den verschiedenen Tetraedern ausschneiden lassen hat nun bei konstanter Summe der Diagonalenlängen dasjenige den grössten Flächeninhalt dessen Diagonale rechtwinklig aufeinanderstehen und gleich lang sind. Dieses ist daher vor den anderen zu Darstellung besonders geeignet.

Als Beispiel ist in Figur 7 das Viereck für das Salzpaar (Ba, Na_2) (SO_4, CO_3) gezeichnet. Die Diagonalen sind gleich lang und die Längen $AL: DL$ und $CL: BL$ stehen im Verhältnis des Molekulargewichts der Salze $Na_2CO_3: BaSO_4$ und $BaCO_3: Na_2SO_4$. Um das Gewichtsverhältnis der Salze zur Darstellung zu bringen, sind von 10: 10% Gerade, parallel den Diagonalen und den Kanten gezogen in der Art wie es die Figur 7 zeigt. Hierdurch lässt sich gleich für jede Mischung das Gewichtsverhältnis in zweierlei Art durch 3 Salze ausdrücken. Im Dreieck ALB hat man Mischungen der Salze: $BaSO_4 + BaCO_3$ und Na_2SO_4 oder Na_2CO_3 ; im Dreieck AIC: $BaSO_4 + Na_2SO_4$ und $BaCO_3$ oder Na_2CO_3 ; im Dreieck BLD: $BaCO_3 + Na_2CO_3$ und $BaSO_4$ oder Na_2SO_4 und im Dreieck CLD: $Na_2SO_4 + Na_2CO_3$ und $BaSO_4$ oder $BaCO_3$.

Um die prozentuale Zusammensetzung zu finden sucht man am besten zuerst das Gewichtsverhältnis auf den Diagonalen und dann das des dritten Salzes auf. Besonders einfach stellt sich bei dieser Darstellung das Gewichtsverhältnis der Bestandteile M' , M'' , S' , S'' , also Ba, Na, SO₄, CO₃ für sich dar. Dieses zeigen die Figuren 8 und 9. Geht man auf das Tetraäder zurück, so werden die auf die vier Bestandteile bezogenen Gewichtsprozente durch Ebenen parallel den Tetraäderflächen dargestellt. Diese schneiden das unregelmässige Viereck in Geraden, die den Seiten parallel sind und bei gleichem Unterschied im Prozentgehalt gleichen Abstand von einander haben. Hieraus folgt folgende Konstruktion: Man berechnet für den Diagonalschnittpunkt L aus der Formel $M'_m M''_o S'_n S''_p$ die Gewichtsprozente an M' , M'' , S' , S'' . Dann teilt man die Lote auf die Viereckseiten derartig ein, dass für die zugehörigen Bestandteile der Punkt L vom Fusspunkte des Lotes aus gerechnet soweit entfernt liegt, wie es dem Prozentgehalt von L entspricht. Man erhält so vier verschiedene Scharen von Parallelen. Der Deutlichkeit halber sind diese auf die beiden Figuren 8 und 9 verteilt.

ERSTER TEIL.

DIE GLEICHGEWICHTE FEST-FLÜSSIG BEI REZIPOREN SALZPAAREN

I. Ein Bodenkörper

Es sollen nun der Reihe nach die Fälle des Gleichgewichtes von Flüssigkeit mit einem, zwei drei und vier Bodenkörpern untersucht werden. Auf Umwandlungerscheinungen, die häufig vorkommen werden, soll keine Rücksicht genommen werden.

Der Fall nur eines Bodenkörpers bei reziproken Salzpaaren tritt dann auf, wenn alle vier Salze einander chemisch sehr ähnlich sind. Dieses ist der Fall, wenn sowohl die Metalle als auch die Säuren mit einander chemisch verwandt sind. Nach den bis jetzt vorliegenden Untersuchungen hat man diesen Fall mit Sicherheit bei den Salzpaaren 1) (Na, K) (Cl, Br); 2) (Na, K) (Cl, I) wahrscheinlich auch bei 3) (Na, Ag) (Cl, Br) 4) (Na, K)

(Br, I) 5) (Cd, Ba) (Cl_2 , Br_2) und vermutlich bei 6) (Pb, Sn) (Cl_2 , Br_2) und 7) (Na_2 , K_2) (SO_4 , CO_3) zu erwarten. (Die Literatur über die bisher untersuchten Mischungen befindet sich am Schluss.)

DIE Z-FLÄCHEN

Die Z-Funktion hat bekanntlich die Definition $Z = E - TS + Pv$, wenn E die innere Energie, S die Entropie, und T, P und v die absolute Temperatur, der Druck und das Volumen sind. Infolge der beiden Hauptsätze der Thermodynamik folgt hieraus $dZ = -SdT + vdp$. Für konstanten Druck ist also $(dZ)_p = -SdT$. Da S positiv ist, so nimmt also in diesem Falle Z mit wachsender Temperatur ab, und mit steigender zu. Hat man homogene Mischungen fester oder flüssiger Körper in jedem Mischungsverhältnis, so zeigt die Z-Funktion einen kontinuierlichen Verlauf. Für das Gleichgewicht sind die Minimumwerte massgebend. In einer graphischen Darstellung zwischen Zusammensetzung der Salzmischungen bei reziproken Salzpaaren und der Z-Funktion erhält man Z-Flächen, wie sie in Figur 10 angegeben sind.

Die Figur gilt für ein Gleichgewicht, bei dem feste Körper noch nicht auftreten können. Die Werte für Z sind räumlich oberhalb des Quadrates aufgetragen. Die Z-Fläche für flüssig liegt alsdann ganz unter der für fest. Beide Flächen berühren die Kanten des Prismas. Erniedrigt man nun die Temperatur so bleiben die Z-Flächen immer konkav nach unten, ändern sich aber sowohl ihrer Form als ihrer Lage nach. Die Z-Flächen-fest rückt nach unten und durchdringt die Fläche-flüssig. Es tritt jetzt eine Gleichgewicht-fest-flüssig auf. Die zugehörigen Mischungen fest-flüssig findet man, wenn man eine Ebene so über die beiden Flächen entlang rollt, dass sie gleichzeitig beide Flächen berührt. Diese berührenden Ebenen führen wie Figur 11 zeigt zu den Berührungsgeraden $l_1 s_1$; $l_2 s_2$ u. s.w., wenn die Ebenen in den Punkten $l_1 l_2 \dots s_1, s_2 \dots$ die Z-Flächen berühren. Man erhält so für die gewählte Temperatur das Gleichgewicht der Salzmischungen fest-flüssig, wie es die Projektion auf die Quadratfläche anzeigt. Bei weiterer Erniedrigung der Temperaturen kommt die Z-Fläche-fest, immer noch unter die Z-Fläche-flüssig zu liegen. Man erhält für tiefere

Temperaturen andere Gleichgewichte fest-flüssig. Schliesslich verlässt die Z-Fläche-flüssig in einen Berührungspunkte die Z-Fläche-fest. Es ist dieses die tiefste Temperatur, bei der noch ein Gleichgewicht-fest-flüssig besteht. Ihrer Lage nach kann die bei niedrigster Temperatur erstarrende Mischung P', wie in dem gewählten Beispiel innerhalb des Quadrates liegen, in anderen Fällen kann sie aber auch auf einer Kante oder Ecke liegen.

Für eine Darstellung von Temperatur-Zusammensetzung kann man ebenfalls ein räumliches Bild bekommen und erhält dann zwei Flächen: eine Erstarrungsfläche und eine Verflüssigungsfläche. Aus beiden ergibt sich die für Dreistoffsysteme bekannte Art des Erstarrens und Verflüssigens einer bestimmten Mischung. Fig. 12 zeigt schematisch die Erstarrungsfläche auf das Quadrat projektiert, wie sie namentlich für (Na, K) (Cl, Br) gilt. Die Annahme einer ternären Minimumtemperatur ist wahrscheinlicher als die dass das Minimum im binären System (Na K) Br die tiefste Erstarrungstemperatur des reziproken Salzpaars ist.

In dem Falle (Na, K) (Cl, Br) wie in anderen Fällen findet im festen Zustande mit fallender Temperatur eine Zerlegung der homogenen Mischkristalle in mehrere andere statt. Die Z-Fläche-fest erhält Falten, die zu Gleichgewichten von mehreren festen Mischkristallen führen. Je tiefer die Temperatur wird umso mehr nähern sich die Mischkristalle in ihrer Zusammensetzung den reinen Salzen. Dieser Fall soll hier jedoch nicht weiter erörtert werden.

Von Interesse sind aber reziproke Salzpaare, mit nur einer Art Mischkristallen, bei denen trotzdem ein binäres Entektikum auftritt. Dieser Fall soll mit Beziehung auf das Salzpaar 8) (Na, Ag) (Cl, J), wo er höchst wahrscheinlich ist, auseinander gesetzt werden. Für den Fall dass bei binären Systemen zwei Mischkristalle gleicher Art auftreten, hat die Z-Funktion-fest eine Form, die die Konstruktion einer Doppeltangente zulässt in der Art wie dieses die rechte Seite des Prismas in der Figur 13 zeigt (H a d e f b G). Hierdurch bildet sich auch auf der Z-Fläche in dem Systeme reziproker Salzpaare eine Falte aus derart, dass man eine Ebene auf der Z-Fläche rollen kann, die diese derart doppelt berührt wie es in Figur 13 bildlich angedeutet ist. Die

labilen Teile im Raume sind weggelassen da sie für das Gleichgewicht keine Bedeutung haben. Es gibt nun Systeme mit zwei verschiedene Arten von Gleichgewichten, je nachdem ob bei Temperaturerniedrigung die Z-Fläche-fest von der Z-Fläche-flüssig ausserhalb oder innerhalb des Flächenstückes a b c durchschnitten wird. Berührt der Flüssigkeitsmantel zuerst ausserhalb a b c, so ist die zugehörige Temperatur höher als die bei der Berührungskegel den Punkt c berührt. Der zugehörige Flüssigkeitspunkt g (in der Projektion g') liegt dann innerhalb a b c. Bei weiterem Durchdringen der beiden Z-Flächen, ändert sich das Gleichgewicht in diesem Teile der Flächen derart, dass sich eine Kurve ausbildet, die die Flüssigkeiten enthält, die gleichzeitig mit zwei festen Körpern im Gleichgewichte sind, wobei die Bodenkörper in ihrer Zusammensetzung andere Kurven durchlaufen. Sucht man das Gleichgewicht zwischen Temperatur und Konzentration auf, erhält man für diesen Teil ein Bild, wie es Figur 14 zeigt die Flüssigkeiten g'l' sind in Gleichgewicht mit den festen Mischungen auf c' a' und c' b'. Ausserhalb des Flächenstückes a c b ist das Verhalten so wie vorher auseinander gesetzt wurde. Das Verhalten beim Erstarren dieser Art Mischungen ist aus dem Diagramm leicht abzulesen. (Vergl. Jänecke, Zeitschrift für physikalische Chemie 67, 1909, 641–668). Fälle dieser Art sind bei Salzmischungen selten.

II. Zwei Bodenkörper

Der Fall des Gleichgewichtes zweier verschiedener Bodenkörper mit Flüssigkeiten in reziproken Salzpaaren liegt vor bei 9) (Na_2 , K_2) (Cl_2 , SO_4) (Jänecke, Zeitsch. f. physik. Chem. 1908). Er ist mit Sicherheit zu erwarten bei den Salzpaaren 10) (Na_2 , K_2) (Cl_2 , CO_3) und zu vermuten bei 11) (Cu_2 , Cd) (Cl_2 , J_2), 12) (K , Ag) (Cl , Br); 13) (Ca , Ba) (Cl_2Br_2); 14) (Ca , Pb) (Cl_2Br_2); 15) (Hg Ag) (Br_2J_2); 16) (Na Jl) (Cl , Br); und anderen.

ABLEITUNG MIT HILFE DER Z-FLÄCHE

Bildet von den vier Salzpaaren des reziproken Salzpaars zwei der in der Figur gegenüberliegende Paare Mischkristalle in un-

beschränktem Masse, die anderen Paare jedoch gar keine, so hat die Z-Fläche-fest eine Form wie es die Figur 15 zeigt. Die Fläche entsteht, wenn eine Ebene auf den Kurven kH und Ei F entlang rollt. Zwischen AB und CB gibt es Mischkrystalle weshalb hier die Z-Funktion durch die Kurven E i F und G k H dargestellt wird, während sie zwischen den Salzmischungen AD und CB durch die Geraden EH und FG angegeben ist. Solange im Gleichgewichte noch kein fester Körper ansteht, liegt die Z-Fläche-fest ganz über der Z-Fläche-flüssig. Bei Erniedrigung der Temperatur durchdringen die beiden Flächen einander und es ergibt sich ein Gleichgewicht zwischen fest und flüssig. Die zugehörigen Mischungen werden erhalten indem eine Ebene auf beiden Flächen rollt. Diese berührt notwendigerweise die Z-Fläche-fest in Punkten die auf den Grenzkurven liegen. Das Gleichgewicht zwischen fest und flüssig ist in der Figur 15 dargestellt. Bei weiterer Erniedrigung der Temperatur rückt die Fläche-flüssig immer höher und berührt schliesslich die Z-Fläche-fest. Diese Berührung die zu der tiefsten Temperatur eines Gleichgewichtes fest-flüssig führt, kann direct in die Z-Fläche oder aber in einem Punkt der Geraden EiF oder GkH eintreten. Es bildet sich also eine Kurve aus, die die beiden entektischen Punkte verbindet, wie es das Erstarrungs Diagramm von Figur 16 zeigt. Auf E F in G befindet sich im Innern des Quadrates (Na_2 , K_2) (Cl_2 , SO_4) ein Minimum der entektischen Kurve. Das Verhalten beim Erstarren wurde an anderer Stelle bereits eingehend auseinandergesetzt. (Jänecke 1.c).

Bilden sich zwischen den Salzpaaren E-H und F-G in beschränktem Masse Mischkrystalle so wird die Z-Fläche etwas anders. An Stelle der Gerade EH und FG treten Kurvenzüge gebildet aus zwei nach unten gehenden krummen Linien und einer an dieser gemeinsamen Tangente. Die Betrachtung wird dadurch etwas anders. Die Punkte die Bodenkörper darstellen, liegen nicht mehr auf den Kanten sondern rücken in das Quadrat hinein.

III. Drei Bodenkörper.

Drei verschiedene Bodenkörper treten wahrscheinlich auf bei der reziproken Salzpaaren 17) (Na, K) (Cl, Fe) 18) (Na, K (Br, Fl; 19) Na, K) (J, Fl) 20) (Na, Ag) (Cl, NO_3) vermutlich auch bei der 21) (K, Ag) (Cl, J) 22) (K_2 , Ag_2) (Cl_2 , SO_4). Eines der vier gleichjonigen Salzpaare bildet dann eine lückenlose Reihe von Mischkristallen Cl (Na K); Br (Na K); J (Na K); Cl (Na Ag); K (Cl, J) und SO_4 (K_2 , Ag_2) während die anderen drei Paare Entektika oder Uebergangspunkte besitzen.

DIE Z-FLÄCHE

Die Z-Fläche hat für diesen Fall eine Form, wie es Figur 17 zeigt. Sie setzt sich aus drei Teilen zusammen: der Ebene E F I und der einseitig gekrümmten Fläche G I F und E I H. Um die Gleichgewichte fest-flüssig zu finden, hat man bei den Temperaturen, wo ein Durchdringen der beiden HZ-Flächen stattfindet die berührende Ebene aufzusuchen. In Figur 17 ist ein Fall angenommen, bei dem die nur teilweise gezeichnete Z-Fläche-flüssig die Z-Fläche-fest nur noch in der Ebene E G J durchschneidet. Die Gleichgewichte, die sich alsdann ergeben sind in der Projektion in das Quadrat A B C D eingezeichnet. Bei weiterer Erniedrigung der Temperatur würde die Z-Fläche-flüssig ein immer kleineres Gebiet der Fläche E G J durchschneiden bis das Flächenstück bei einer bestimmten Minimumtemperatur in einem Punkte zusammengeschrumpft ist. Man erkennt, dass sich für verschiedene Temperaturen Gleichgewichtspunkte zwischen Flüssigkeit und zwei festen Körpern ergeben, die von, vom Minimumpunkt g nach den drei entektischen Punkten a, b und c laufen. Im Punkte g bildet sich ein ternäres Entektikum heraus. Bei der Minimumtemperatur desselben besteht das invariante Gleichgewicht zwischen Flüssigkeit und drei festen Körpern, nämlich der beiden Salzen A und C und einer isomorphen Mischung, die zwischen B and D liegt. Dieser Fall wird beim Vorkommen dreier fester Phasen der weitaus häufigste sein. Das Erstarrungsbild zeigt dann Figur 18.

Ein anderer Fall tritt ein, wenn die Z-Fläche-flüssig bei der

tiefsten Temperatur ausserhalb der Eben E F J durchschneidet. Ein solcher Fall ist wahrscheinlich beim Auftreten eines binären Uebergangspunktes, kann aber bei drei binären Entektika auch vorkommen. Es besteht hier also ein Unterschied gegenüber einem einfachen ternären Gemisch mit drei Entektika, da sich in diesem Falle stets ein ternäres Entektikum bildet. Die Figuren 19 und 20 deuten die auftretenden Gleichgewichte an, wobei Figur 20 noch die Annahme ternärer Mischkrystalle gemacht ist. Die Z-Fläche-fest hat alsdann eine kompliziertere Form, enthält aber stets ein ebenes Dreieck. Ist die Temperatur so gewählt, dass die Z-Fläche-flüssig von der Ebene dieses Dreiecks berührt wird, so hat man ein invariantes Gleichgewicht zwischen einer Flüssigkeit und drei festen Körpern, eben der durch die Dreieckspunkte dargestellten Mischungen. Das Verhalten beim Erstarren ist aus Bekanntem leicht zu übertragen. In Figur 19 ergeben z. B. Mischungen innerhalb des Dreiecks D E C beim Erstarren, bei der Temperatur des invarianten Gleichgewichtes eine Mischung aus der Flüssigkeit C dem festen Salze A und einen der beiden festen Körper D oder E. Bei weiteren Entziehen von Wärme bleibt die Temperatur solange konstant, bis das Salz A vollständig verschwunden ist, indem sich eine Umsetzung nach der (qualitativen) Gleichung $C+A=D+E$ vollzieht.

Es würde zu weit führen, weiter auf diese Gleichgewichte einzugehen. Es soll nur der Vollständigkeithalber noch ein Fall erwähnt werden, der möglich ist, obwohl er selten auftreten wird, weil alsdann in zwei benachbarten binären Salzmischungen Uebergangstemperaturen vorhanden sein müssen. Dieser Fall der ternären Mischkrystalle vorausgesetzt, tritt auf wenn im invarianten Gleichgewichte einer der *festen* Körper, seiner Zusammensetzung nach, innerhalb eines Dreieckes liegt, gebildet aus der Flüssigkeit und den beiden anderen festen Körpern des Gleichgewichtes.

IV. Vier Bodenkörper

Der weitaus wichtigste Teil bei reziproken Salzpaaren ist der mit vier Bodenkörpern. Dieses wurde von mir bereits an anderer Stelle eingehend behandelt, jedoch ohne Benutzung der Z-Funktion, was hier nachgeholt werden soll (Jänecke 1.c).

Die Z-Funktion. Bilden sich gar keine Mischkristalle, so kommen für das Gleichgewicht nur die Werte von Z für die festen Salze in Betracht. Haben diese die in Figur 21 durch die Punkte E G F H dargestellt sind, so hat man sie zur Bildung der Z-Fläche-fest durch Ebenen zu verbinden. Es liegen dann die Potentiale von Mischungen des einen reziproken Salzpaars (FH) unter denen der übrigen Mischungen. Da nun für das Gleichgewicht nur die Minimumwerte der Z-Funktion gelten, ist dieses Salzpaar gegenüber den anderen ausgezeichnet. Es wird das stabile Salzpaar genannt. Die Gleichgewichte findet man wiederum aus den Durchdringungen der Z-Fläche-flüssig mit beiden Ebenen, die in diesem Fall die Z-Werte-fest darstellen. In Fig. 21 ist wieder ein Fall konstruiert, bei dem in Grenzmischungen keine Gleichgewichte mehr von fest und flüssig auftreten. Das in diesem Falle vorhandene Gleichgewicht ist durch die Flüssigkeitskurve e f g h angegeben. Bei weiteren Heraufrücken der Flüssigkeitsfläche findet erst eine Berührung der Geraden F H und dann eine solche der beiden Z-Ebenen-fest statt. Es findet also in diesem Falle eine vollständige Zerlegung in zwei ternäre Gleichgewichte zwischen A D B und B D C statt, wie es die im Quadrat A B D C liegenden Kurven zeigen.

Ein anderer Fall ist der, dass die Z-Fläche-flüssig bei einer bestimmten Temperatur die Ebene einer der beiden Dreiecke E H G oder E H F ausserhalb dieser Flächen berührt. Das sich hierbei ausbildende invariante Gleichgewicht führt zu einem ternären Uebergangspunkt. Dieses Gleichgewicht ist in Figur 22 dargestellt. Das Zustandsdiagramm ist im Quadrat A B C D angegeben.

Es besteht demnach im Gegensatz zu einfachen Dreistoffsystemen mit binärer Entektika die Möglichkeit des Auftretens eines ternären Uebergangspunktes. Dieser Fall ist dann wahrscheinlich, wenn der Schmelzpunkt eines der Salze des instabilen Salzpaars besonders hoch ist und die Schmelzpunkte des stabilen Salzpaars einander nicht zu nahe liegen.

Der Fall, dass alle vier Salze am Gleichgewichte beteiligt sind, wird bei Mischungen auftreten, in denen weder die Metalle noch die Säurereste chemisch besonders stark mit einander verwandt sind, jedoch auch einander nicht so fern stehen, dass sich

Doppelsalze bilden. Solche Mischungen sind Carbonate mit Sulfaten oder Nitraten, Chloride mit Carbonaten, Sulfaten oder auch Jodiden und anderen.

V. Mehr als vier Bodenkörper

Hat man reziproken Salzpaaren mehr als vier Bodenkörper, so ergeben sich Fälle, die bereits an ternären Systemen eingehend untersucht wurden. Besonders hat Schreinemakers in dem dritten Hefte des Buches von Roozeboom über Phasenlehre auseinandergesetzt. Man kann also derartige Systeme unter Mitbenutzung des hier auseinander-gesetzten zur Darstellung bringen. Ein Fall ist in der Figur 23 dargestellt. Hierbei sind Wasser, Säure und Oxyd als Salze, $M'S' M'S''$ und $M_2'S'$ behandelt. Die Gleichgewichte fest-flüssig beziehen sich auf die Temperatur von 30° . Sie wurden durch Löslichkeitsuntersuchungen festgelegt.

ZWEITER TEIL

Doppelt-ternäre Salzmischungen

Doppelt-ternäre Salzmischungen sollen solche genannt werden, die sich aus den sechs verschiedenen Salzen bilden lassen, die in den beiden allgemeinen Formeln $(M'M'')$ ($S'S''S''$) oder $(M'M''M'')$ ($S'S''$) enthalten sind. Die sechs Salze sind also in einem Falle $M'S'$, $M'S''$, $M'S''$ und $M''S'$, $M''S''$, $M''S''$ und im anderen Falle $M'S'$, $M''S'$, $M''S'$ und $M'S''$, $M''S''$, $M'''S''$. Doppelt-ternär nenne ich die Mischungen weil sich aus den sechs Salzen immer zwei ternäre Systeme bilden lassen, die sich entweder nur in den positiven oder nur in den negativen Bestandteilen der Salze unterscheiden.

Bei meiner neuen Darstellungsform der Untersuchung van't Hoff's über ozeanische Salzablagerungen habe ich auf diese Salzmischungen kurz hingewiesen (Zeitschrift für anorganische Chemie 53, 1907, 319-326), sonst sind sie wohl noch niemals behandelt worden. Die Untersuchung dieser Art Mischungen kann hier nur flüchtig angedeutet werden. Ihr Umfang ist zu gross.

Mischungen dieser Art kommen durch in einem dreiseitigen Prisma zur Darstellung wie es Figur 24 zeigt. Die drei Koordinaten-Achsen sind A B, A C und AD, indem AB und AC einen Winkel von 60° mit einander bilden, während AD senkrecht auf der Ebene dieser Geraden steht. Sind die Koordinaten eines Punktes auf diese Achsen bezogen x , y und z so soll ein hierdurch dargestellter Punkt eine Salzmischung darstellen, die man durch die Formel $S_x''S_y'''S_{(1-x-y)}'M_z''M_{(1-z)}'$ ausdrücken kann. Variiert man die Werte von x , y und z zwischen Null und Eins, so lassen sich alle Mischungen aus den sechs Salzen zur Darstellung bringen. Man erkennt, dass die Begrenzungsflächen des Prismas den beiden ternären Salzmischungen und den drei reziproken Salzpaaren entsprechen, die man aus den sechs Salzen bilden kann. Die doppelt-ternären Salzmischungen werden damit zu einem quaternären System, da sie durch eine räumliche Darstellung umfasst werden können.

Es soll nun bewiesen werden, dass eine Mischung, die sich aus zwei beliebigen anderen Mischungen bilden lässt in der räumlichen Darstellung auf der Verbindungsgeraden liegt, deren Eckpunkte diese beiden Mischungen angeben. Hat man zwei Mischungen P_1 und P_2 mit den Formeln: $S_{x_1}'''S_{y_1}''S_{(1-x_1-y_1)}'M_{z_1}''M_{(1-z_1)}'$ und $S_{x_2}'''S_{y_2}''S_{(1-x_2-y_2)}'M_{z_2}''M_{(1-z_2)}'$ und man vermischt dieselben in den Molekulverhältnis aP_1+bP_2 so entsteht daraus nP wenn eine gewisse Zahl und P eine Mischung $S_x''S_y'''S_{(1-x-y)}'M_z''M_{(1-z)}'$ ist. Wenn man jetzt die Mengen der zusammensetzenden Bestandteilen denen des entstandenen Salzes gleichsetzt, so erhält man die fünf Gleichungen:

$$nx = ax' + bx''$$

$$ny = ay' + by''$$

$$n(1-x-y) = a(1-x'-y') + b(1-x''-y'')$$

$$nz = az' + bz''$$

$$n(1-z) = a - az' + b + bz''$$

Die ersten beiden Gleichungen in Verbindung mit der dritten oder die vierte Gleichung in Verbindung mit der fünften ergibt $n = a + b$ und hieraus folgt:

$$x = \frac{a}{a+b} x_1 + \frac{b}{a+b} x_2$$

$$y = \frac{a}{a+b} y_1 + \frac{b}{a+b} y_2$$

$$z = \frac{a}{a+b} z_1 + \frac{b}{a+b} z_2$$

Nach den Regeln der analytischen Geometrie bedeutet dieses, dass Punkt P auf der Geraden P_1P_2 liegt und zwar in einem Punkte der die Gerade im Verhältnis $a:b:b$ teilt. Dann muss auch dass eine Mischung hergestellt aus drei verschiedenen Salzmischungen in der Darstellung in einem Punkte der Ebene liegen, die durch diese drei Punkte gebildet werden kann.

Aus dieser linearen Beziehung folgt, dass man die Beziehungen die man für die Darstellung quaternären Mischungen im Tetraäder kennt auf diese prismatische Darstellung übertragen kann.

Es sollen nun ganz kurz die Gleichgewichte fest-flüssig zwischen Flüssigkeit und einen bis sechs Bodenkörper behandelt werden.

EIN BODENKÖRPER

Einen Bodenkörper hat man bei doppelt-ternären Salzmischungen dann zu erwarten, wenn alle Salze mit einander isomorph sind. Ein solcher Fall liegt vor bei 23) (Na K) (Cl Br J) vermutlich auch bei 24) (Cl Br) (Sn Pb Ba). Einige andere Fälle in denen ebenfalls Isomorphie herrscht obwohl sich Entektika zeigen sind unten kurz erwähnt.

Die Z-Funktion. Ebenso wie bei ternären Mischungen und reziproken Salzmischungen wird auch bei doppeltternären Salzmischungen die Z-Funktion für fest und flüssig benutzt um die Gleichgewichte zu finden. In dem dreiseitigen Prisma bildet die Z-Funktion für fest-flüssig je ein skaleres Feld aus, derart dass die Z-Werte stetig in die Grenzwerte auf den Begrenzungsfächen übergehen. Bei vollständiger Mischbarkeit in festem Zustande ist das Z-Feld-fest ähnlich gebaut wie das Z-Feld-flüssig. Man kann sich die Felder vorstellen, als eine Reihe in einandergesteckter Bälle, die von den Grenzflächen gerade abgeschnitten sind, wobei jeder Ball einen gewissen Wert des thermodynamischen Potentials besitzt. Die Bälle muss man sich in anderen Fällen als schlauchartig deformiert vorstellen oder auch so, dass nur noch übereinanderliegende nicht geschlossene Flächen

vorkommen. Für jede Temperatur verändert sich das Z-Feld sowohl seiner Form als auch seinen absoluten Werten nach. Bei einer bestimmten Temperatur hat man demnach zwei Z-Felder für fest und flüssig die einander durchdringen. Ein Gleichgewicht festflüssig ist für die gewählte Temperatur nur möglich, wenn der kleinsten Werte Z-flüssig kleiner ist als der kleinste Wert Z-fest und wenn anderseits der grösste Wert Z-flüssig grösser ist als der grösste Wert Z-fest. Ist dieses nicht der Fall, so hat man bei der gewählten Temperatur entweder nur feste Mischungen (Z-fest an allen Stellen im Raume kleiner als Z-flüssig) oder nur flüssige Mischungen (Z-fest überall grösser als Z-flüssig). Besteht nun ein Gleichgewicht fest-flüssig so findet man die zugehörigen Gleichgewichtswerte als Berührungs-punkte gewisser Ebenen an Flächen der beiden Z-Felder. Eine solche Berührungsgerade durchschneidet beide Z-Felder. Sind nun Z_1 und Z_2 die Werte für Z-flüssig und Z-fest, die den be-rührten Flächen flüssig und fest zukommen, so ist zunächst Z_1 kleiner als Z_2 . Damit die Geraden Berührungsgeraden sind müs-sen ferner die linear interpolierten Werte zwischen Z_1 und Z_2 kleiner sein als die beiden Werte für Z auf diesen Geraden die dem Z-Feld-flüssig und dem Z-Feld-fest zukommen.

Eine genaue mathematische Behandlung kann hier nicht gegeben werden man erkennt aber, wenn man alle Tangenten bei den gewählten Temperaturen zieht, dass die zugehörigen Werte für fest-und flüssig auf zwei Flächen im Innern des Prismas liegen. Nimmt man nun die Gleichgewichte fest-flüssig für alle Temperaturen zusammen so erhält man auch zwei Felder für fest und flüssig die in ganz bestimmter Art mit der Tempe-ratur und Zusammensetzung in Beziehung stehen. Einer jeden Temperatur entsprechen zwei einander umschliessenden Flächen für fest und flüssig. Von Wichtigkeit ist noch die Lage des Mi-nimumpunktes. Da es notwendigerweise eine Minimumtem-pe-ratur gibt, und die Flächen einander umschliessen, muss die Minimumtemperatur einen Punkt darstellen, der beiden Gleich-ge wichts-Feldern fest und flüssig gemeinsam ist. Dieser Mi-nimumpunkt wird vielfach im Innern des Prismas liegen, er kann aber auch in besonderen Fällen einer Begrenzungsfläche, be-grenzenden Ecke oder in einen Eckpunkt fallen. Für (Na, K)

(Cl, Br, J) ist er jedenfalls im Innern des Prismas zu suchen. Möglich ist allerdings hierbei, dass durch die Entmischungsvorgänge im festen Zustande eine Störung auftritt. Es bilden sich alsdann Gleichgewichte aus, die zu den unten auseinandergestzten Fällen Beziehung haben. Beim Abkühlen zeigen alle Mischungen in dem oben angegebenen Fall nur ein Erstarrungsintervall.

In folgenden Fällen sind Komplikationen trotz vollständiger Isomorphie zu erwarten. 25) (Na, Ag) (Cl, Br, J); 26) (Cl, Br) (Na, K, Ag) und 27) (Cl, J) (Na, K, Ag). Bei 25) ist vermutlich von den neun begrenzenden Kanten das System Ag (Cl J) ein binäres System mit Entektikum. Hieraus folgt, dass sich in dem Prisma ein räumliches Gebiet ausbildet in dem zwei Bodenkörpern möglich sind. Bei 26) sind wahrscheinlich (K, Ag) Cl und (K, Ag) Br binäre Systeme mit Entektikum. Es wird sich deshalb ein räumliches Gebiet mit zwei Bodenkörpern aus dem Prisma ausbilden, das durch das ganze Prisma geht. Noch grösser muss dieses bei 27) sein, so wahrscheinlich drei binäre Entktika vorkommen, nämlich (K, Ag) Cl, (K, Ag) J und Ag (Cl, J). Zur Ableitung derartiger Fälle muss man sich das vorhergehende Bild der ineinandersteckenden Bälle derart verändert denken, dass die Ballsysteme für Z-fest und Z-flüssig Beulen erhalten hat.

ZWEI BODENKÖRPER

Bei zwei Bodenkörpern sind zwei Fälle zu unterscheiden, die durch die Figuren 25 und 26 angedeutet sind. Bei den Mischungen die auf eine Darstellung nach Figur 25 führen hat das thermodynamische Feld für Z-fest eine Art schlauchförmige Gestalt. Konstruiert man für eine bestimmte Temperatur wie wieder die Gleichgewichtstangenten so erhält man durch Verbindung der zugehörigen Punkte fest und flüssig Flächen, die einander zugehören. Die Flächen die sich auf die Bodenkörper beziehen, sind die begrenzenden Dreiecksebenen des Prismas, während die Flüssigkeitsflächen innerhalb des Prismas liegen. Eine solche Fläche ist in Figur 15 an der Seite D E F angedeutet. Bei einer bestimmten Temperatur hat man immer zwei solcher

Flächenpaare, die zu be den Seiten von G H J liegen. Bei hoher Temperatur kann eines der Paare verschwinden. Bei tiefer Temperatur dagegen fallen die beiden Paare in einer Kurve auf der Fläche G H J zusammen. Die beiden Flüssigkeitsflächen bilden dann eine Linse, die auch von den Quadratflächen gerade abgeschnitten sein kann. In Figur 25 ist auf der rechten Seite ein Teil des Gleichgewichtes fest-flüssig dargestellt. Betrachtet man das Gesamtgleichgewicht fest-flüssig so erhält man auf der krummen Fläche G H J ein System von einander umschließenden Isothermen für die den flüssigen Mischungen bei den zugehörigen Temperaturen. Die zugehörigen festen Mischungen liegen die auf den das Prisma begrenzenden Dreiecken liegen. Im Fall einer Minimumtemperatur liegen die drei Zugehörigen Mischungen, die flüssige und die beiden festen Mischungen auf einer Geraden. Die Endpunkte auf den Dreiecksflächen entsprechen den festen Mischungen des Gleichgewichtes, während die mit der Flüssigkeit dargestellt durch den Durchschnittspunkt der Geraden mit der Fläche G H J dargestellt wird. Die Minimumtemperatur wird häufig im Innern der Fläche G J H liegen, so kann aber auch auf eine der Quadratflächen oder eine der Kanten zu liegen kommen. Nach den bisher vorliegenden Untersuchungen kann man kein System angeben wo dieser Fall mit Sicherheit auftreten wird. Es ist hierbei erforderlich, dass die drei gleichartigen Formen der doppelt ternären Salzmischung einander chemisch nahe stehen, sodass in den beiden ternären Systemen $M'(S'S''S'')$ und $M''(S'S''S'')$ vollständige Isomorphie herrscht. M' und M'' müssen einander chemisch ferner stehen, sodass drei binäre Entektika bei $(M'M'')S'$, $(M'M'')S''$ und $(M'M'')S'''$ vorhanden sind.

Der zweite Fall zweier Bodenkörper ist durch Fig. 26 angedeutet. Er ist zu erwarten bei $(Na_2K_2)(Cl_2, Br_2, SO_4)$ und $(Cl_2, Br_2)(Ba, Pb, Ca)$. Man hat hierbei ein reziprokes Salzpaar $(Na, K)(Cl, Br)$ und $(Cl_2, Br_2)(Ba, Pb)$ das vollständige Isomorphie zeigt.

Das Z-Feld-fest hat eine eigentümliche Form. Es läuft von der Kante B C nach der gegenüberliegenden Quadratfläche A D C F. Man erhält als Gleichgewicht fest-flüssig für eine bestimmte Temperatur wie vorher wieder zwei Gebiete von

denen aber hier das eine der Kante BE und das andere der Fläche A D C F benachbart ist. Die zugehörigen festen Mischungen liegen auf dieser Kante oder in dem Quadrate. Bei tieferer Temperatur berühren sich die Flüssigkeitsflächen in Kurven die auf einer Fläche G H J K liegen. Auf dieser Fläche lassen sich Flüssigkeitsisothermen konstruieren, die für verschiedene Temperaturen durch einander umschliessende Kurven dargestellt sind. Der Minimumtemperatur entspricht wieder ein Gleichgewicht zweier fester Körper mit Flüssigkeit das sich durch eine Gerade darstellen lässt.

Die Erstarrungsvorgänge in beiden skizzierten Fällen sind ähnlich. Alle Mischungen in Prisma führen nach Ausscheidung einer festen Mischung zu einer Flüssigkeit auf den Flächen G H J (Figur 25) oder G H J K (Fig. 26). Dann folgt die Ausscheidung einer zweiten festen Mischung, worauf unter gleichzeitiger Ausscheidung zweier Bodenkörper das Gleichgewicht sich so ändert dass die flüssige Mischung stets auf diesen Flächen liegt bis alles zu einer Mischung zweier fester Körper erstarrt ist. Die Flächen G H J und G H J K kann man entektische Flächen nennen.

DREI BODENKÖRPER

Beim Auftreten dreier Bodenkörper in doppelt—ternären Salzmischung kann man drei Fälle unterscheiden die durch die Figuren 27, 28 und 29 dargestellt sind. In diesen Fällen gibt es unter den 9 binären Mischungen drei oder vier die vollständige Mischbarkeit in festem Zustande zeigen. Die Lage dieser Mischungen zeigen die Figuren an.

Wenn man in diesen Fällen die Tangentenebenen an die beiden Z-Felder aufsucht, erhält man drei verschiedene Gebilde, die in den drei räumlichen Gebieten des Prismas liegen. Die festen Phasen befinden sich auf den das Prisma begrenzenden Kanten oder Ebenen während die flüssigen Phasen Flächen im Innern des Prismas ergeben, die bis an den Kanten gehen oder sich auch vorher schliessen. Bei tieferen Temperaturen berühren sich diese Gebiete in Kurven die auf den drei im Innern des Prismas liegenden Flächen liegen, die die Kurve a b gemeinsam haben. Auf dieser Kurve oder in einem ihrer Eckpunkte liegt auch die

Minimumtemperatur des Gleichgewichtes zwischen drei festen Phasen und Flüssigkeit. Die Kurve a b ist eine räumliche entektische Kurve und stellt ein monovariantes Gleichgewicht dar. Befindet sich auf ihr eine Minimumtemperatur, so liegen die drei festen Phasen des Gleichgewichtes mit dem Minimumpunkt in einer Ebene. Beim Erstarren der durch diesen Minimumpunkt dargestellten Mischung scheiden sich gleichzeitig drei feste Mischungen konstanter Zusammensetzung aus.

Das Erstarren sämtlicher Mischungen im Innern des Prismas findet bei Temperaturen statt die der Kurve a b zukommen. Die Mischungen zeigen drei Verzögerungen in den Abkühlungskurven, entsprechend der aufeinander folgenden Ausscheidungen eines, zweier und dreier Bodenkörper.

Der durch Figur 28 angegebene Fall ist bei 30) (Na, K) (Cl, Br, Fl) und 31) (Na, K) (Br, J, NO₃) wahrscheinlich der durch Figur 29 dargestellte Fall bei 32) (Na₂, Pb) (Cl₂, Br₂, J₂) 33) (Na₂, Ca) (Cl₂, Br₂, J₂).

VIER BODENKÖRPER

Besonders interessant wird sich bei doppelt-ternären Salzmischungen der Fall stellen bei dem vier Bodenkörper zu erwarten sind. Vermutlich zeigen die Salzmischungen 34) (Ca, Ba) (Cl₂, Br₂, J₂) und 35) (Cd, Pb) (Cl₂, Br₂, J₂) derartiges Verhalten.

In den Figuren 30 und 31 ist angegeben wie die Lage der Mischungen auf den Grundflächen sein kann, und in welcher Art das Prisma hierbei in vier Teile zerlegt wird. Bei Figur 30 kann noch durch eine Diagonal-Fläche eine Zerlegung in zwei räumliche Gebiete, ein Tetraeder und eine Pyramide bewirken. In jedem dieser Gebiete bildet sich alsdann eine räumliche entektische Linie aus (ad und cb). Das Verhalten derartiger Mischungen ist durch den vorhergehenden Fall dreier Bodenkörper erklärt.

Möglich ist aber auch der in Figur 31 angegebene Fall, der zu meinen quaternären Entektikum (e) einem Gleichgewicht vier feste Phasen mit einer Flüssigkeit führt. Die vier festen Phasen sind alsdann die beiden Salze C und F und die beiden Mischungen g und h. Der Punkt e muss innerhalb des Tetraeders C F g h

liegen. Das Erstarren aller Mischungen in diesen Tetraedern endet in diesem invarianten Punkte während die Mischung ausserhalb des Tetraeders B E G H auf den von e ausgehenden Geraden zu Mischungen dreier fester Körper erstarrt. Vorausgesetzt ist beim Erstarren stetes Gleichgewicht zwischen Bodenkörper und Schmelze.

FÜNF BODENKÖRPER

Der verhältnismässig selten vorkommende Fall von fünf Bodenkörpern (vielleicht bei 36) (K_2 , Ag_2) (SO_4 , Cl_2 (NO_3)₂) soll nicht weiter erörtert werden.

SECHS BODENKÖRPER

Von Interesse ist der häufig vorkommende Fall von sechs Bodenkörpern nämlich der sechs Salzen des Systemes bei den doppelt-ternären Salzmischungen. Ich habe an anderer Stelle hierauf bereits kurz hingewiesen. (Jänecke 1.c.) Die Z-Funktion-fest ist in diesem Falle für jede Temperatur aus den Z-Werten der festen Salze für diese Temperatur räumlich zu interpolieren. Aehnlich dem vorher auseinandergesetzten Fall bei reziproken Salzpaaren mit vier Bodenkörper, kann man in verschiedener Art die 6 Eckpunkte zusammenfassen. In jedem Falle hat man aber dreimal vier Punkte die drei Tetraedern entsprechen, in denen die Z-Funktion kleiner ist als bei anderer Zerlegung des Prismas. Bei Hinzunehmen der Z-Funktion flüssig erhält man die Gleichgewichte fest-flüssig und diese führen zu drei invarianten Mischungen zwischen drei Flüssigkeiten mit den vier durch die Tetraedereckpunkte dargestellten Salzen. Liegen die drei Flüssigkeiten innerhalb der drei Tetraeder in die das Prismas zerlegt ist, so hat man für jedes Tetraeder das bekannte Verhalten der Mischungen vier Komponenten mit einem quaternären Entektitum. Dieses zeigen die beiden Figuren 32 und 33. Es kann aber auch der Fall eintreten, dass die Flüssigkeit nicht im Innern des Tetraeder liegt mit dessen Eckmischungen sie ein invariantes Gleichgewicht bildet. Man hat alsdann einen quaternären Uebergangspunkt. In diesem Falle ist für ein gewisses Gebiet

des Prismas das Verhalten durchaus dem von Mischungen dreier Stoffe mit einen Uebergangspunkt ähnlich.

Sechs Bodenkörper treten vermutlich bei den Salzmischungen 37) (Ca, Ba) (Cl₂, J₂, SO₄) und anderen auf.

Ein weiteres Eingehen würde hier zu weit führen.

MEHR ALS SECHS BODENKÖRPER

Es wird sehr viel Systeme geben mit mehr als sechs verschiedenen Bodenkörpern. Die Gestze sind leicht zu übersehen, wenn man das vorhergehende sinngemäss anwendet. Betracht man wie anfangs erwähnt auch H₂O und HCl als Salze M'S' und M'S'' so ist bereits ein Fall dieser Art von Schreinemakers untersucht nämlich das Gleichgewicht (Ba, H₂, Na₂) (Cl₂ O) bei 30°. Man hat in diesem Falle eine ganze Anzahl Verbindungen der Komponenten. Schreinemakers führt seine Darstellung auf eine vierseitige Pyramide zurück und kommt dann nebenher auch zu einem allerdings schiefwinkeligen Prisma. Bei Darstellung mit einem rechtwinkeligen Prisma gewinnt die Darstellung der Resultate an Deutlichkeit.

In solchen Systemen kann es auch noch invariante Gleichgewichte mit Uebergangspunkte anderer Art geben. Auch Mischkrystalle können das Verhalten komplizieren.

Auf alles dieses soll später einmal an anderer Stelle eingegangen werden.

EINIGE LITERATUR ÜBER BINÄRE SALZCHMELZER

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ZUSAMMENFASSUNG

- 1) Es wurden die Beziehungen zwischen Gewichtsprozenten und Molekülprozenten bei reziproken Salzpaaren auseinander-gesetzt und eine Darstellung bezogen auf Gewichtsverhältnisse gegeben.
- 2) Die Gleichgewichtsverhältnisse fest-flüssig bei reziproken Salzpaaren wurden unter Benutzung der Z-Funktion bei einem, zwei, drei, vier und fünf und mehr Bodenkörpern auseinander-gestzt.
- 3) In allen Fällen wurden Beispiele angeführt von Salzmischungen die voraussichtlich das angegebene Verhalten zeigen.
- 4) Die Gleichgewichte für doppelt-ternäre Salzmischungen $(M'M''M''')$ ($S'S''$) oder $(M'M'')$ ($S'S''S'''$) für einen bis sechs und mehr Bodenkörper wurden in ähnlicher Weise kurz ausein-ander-gesetzt.

THE INCLUSIONS IN ELECTROLYTIC SILVER AND THEIR EFFECT ON THE ELECTROCHEMICAL EQUIVALENT OF SILVER

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SUMMARY

(1) An apparatus has been devised by means of which the volatile inclusions in electrolytic silver can be separated from the silver and determined. The method is based on the solution of the silver in molten tin.

(2) It has been shown that electrolytic silver from the purest silver nitrate solution gives off appreciable quantities of gases when dissolved in molten tin, and that the amount liberated depends on the purity of the silver nitrate solution.

(3) A method of analysis of the small quantities of gases has been devised, based on the principle of fractional condensation.

(4) The gases liberated are water vapor, carbon dioxide, nitrogen, and small quantities of carbon monoxide and hydrogen.

(5) The total quantity of impurity in electrolytic silver deposited from the purest silver nitrate solution is at least 0.05 mg. per gram silver.

(6) There is no evidence of selective absorption of silver nitrate by silver crystals deposited from pure silver nitrate solutions. There is selective absorption from impure solutions.

(7) A negative correction of at least 5 parts in 100,000 must be applied to the electrochemical equivalent of silver as determined by Smith, Mather, and Lowry.

STUDIES IN THE SPEED OF REDUCTIONS

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For some years past, I have been conducting experiments to ascertain whether certain phenomena due to the mixture of derivatives of closely allied bases might not indicate the formation of complex bases of a higher order, similar to the well-known complex acids. The difference in the colloidal tendencies of mixed and pure basic salts, the appearance of spectroscopic lines in a mixture of oxides, none of which omit these lines in a pure state, the curious relation of Thorium & Cerium, with respect to incandescence are among the phenomena which might call for such an explanation. While my experiments have so far failed to yield positive evidence in this direction, I have obtained certain results which seem worth recording for their own sake.

My first attempts concerned themselves with the possible formation of an Aluminic-Ferric complex, by the hydrolysis of the mixed chlorides. Solutions representing systematic variations in concentration and relative proportion of Ferric & Aluminic Hydroxides were observed for several years and finally analyzed, with the result that I am convinced that no Aluminum is carried down permanently combined with basic ferric chlorides. Any temporary occlusion is compensated on standing with the supernatant acid solution of ferric chloride.

But a complexity of these two bases might be indicated, if the behavior of Ferric Chloride toward reducing agents were affected by Aluminic Chloride especially since the latter would hardly be likely to figure as a chlorine-carrier in dilute solutions. When these experiments yielded a positive result, other chlorides were mixed with ferric chloride to test their effect upon its stability toward reducing agents. The method followed closely that employed by A. A. Noyes, in studying the speed of reaction between Ferric Chloride & Stannous Chloride. He mixed dilute

solutions of these two salts in equivalent proportions, drew measured samples from time to time, running them into a solution of mercuric chloride, to arrest the reaction by removing all the remaining stannous chloride without affecting the trivalent iron; then determining the amount of the latter by titration with potassium dichromate. Using twentieth normal solutions of these two compounds, I obtained constants for the reaction agreeing closely with Noyes' figures, upon adding Aluminic Chloride, also in twentieth normal concentration, the speed was more than doubled; while it was quadrupled in the presence of a tenth normal solution of Aluminic Chloride. Of course, such a result might be ascribed to the excess of chlorine ions present, especially as Noyes had found that Hydrochloric Acid has an effect, though of a different kind. If so, chlorides of divalent elements should not have as great an effect: yet 1/20 normal solutions of Manganous Chloride and of Glucinic Chloride also double the speed of reduction, although the ionization cannot be the same. A 1/20 normal solution of quadrivalent Thorium does not accelerate quite as much.

As is well-known, Noyes considers this as a typical reaction of the third order, and shows that his equation

$$c_3 = \frac{1}{2r} \left(\frac{1}{(A-X)^2} - \frac{1}{A^2} \right)$$

applied to his experimental data, gives a fairly constant value for c_3 . My series, which I cannot reproduce in full, show about the same degree of constancy for c_3 . Consequently, I think it fair to assume that the reaction remains of the same type, and that the variations in speed are due to the specific influences of the metals concerned. For, as will be seen, the accelerations are not exactly the same. I give average values of c_3 , always for the reaction between 1/20 normal Ferric & Stannous Chlorides.

| | c_3 |
|---------------------------|-------|
| Without admixture | 67.8 |
| With 1/20 AlCl_3 | 149.6 |
| With 1/20 MnCl_2 | 161.2 |
| With 1/20 GlCl_2 | 159.4 |

| | |
|-----------------------------|-------|
| With 1/20 ThCl ₄ | 157. |
| With 1/10 AlCl ₃ | 288.1 |
| With 1/10 MnCl ₂ | 266.4 |
| With 1/20 SnCl ₄ | 225. |
| With 1/40 SnCl ₄ | 131. |

The last two values are anomalous; but expectedly so, as this compound enters into the original reaction.

Noyes has found that the addition of free hydrochloric acid alters the nature of the reaction, so that it becomes one of the second order. I find that several chlorides, notably Zirconium Chloride and Oxychloride have a similar effect. The reason must be different from Noyes' explanation, based on free chlorine ions.

Another series of experiments, with the same fundamental object, sought to study the influence of analogous compounds on Ceric Sulphate. Cerium, alone of the so-called rare-earth group, lends itself to studies in oxidation and reduction, although virtually no work has been done in following these changes quantitatively. Of the salts of the tetravalent base, only the sulphate is stable in aqueous solution, and then only in the presence of much free acid. On standing, its orange color fades very slowly, a marked odor of ozone indicating the by-product of its reduction to the cerous state. Indeed, I am doubtful whether I have ever had a solution of the tetravalent salt, free from any trivalent admixture. After many trials I found that a fair idea of a reduction speed might be obtained by mixing ceric sulphates and glucose in equimolecular amounts in dilute solution, maintaining at 25° C., and titrating samples with very dilute hydrogen dioxide solution, which instantaneously completes the decolorization of the ceric salt. The reaction with glucose is completed in about two hours and can be readily followed in 15 minute intervals. Of course, the stability of the hydrogen peroxide standard was meanwhile controlled with permanganate solution.

For some unexplained reason, the reaction as studied by me does not follow a logarithmic law: the amount of cerium reduced is simply proportionate to the elapsed time, so that t/x is pretty nearly constant for every individual series. So anomalous a

behaviour naturally precludes any claim on rigid deduction. But the experiments had comparative values, when they were compared with others, in which equivalent quantities of Lanthanum Sulphate and Thorium Sulphate had been mixed with the Ceric solution.

| Values of $x/tx 10$ | |
|---------------------|---------------|
| Pure Ceric solution | 694.8, 693.1, |
| With Thorium | 708, 697 |
| With Lanthanum | 665.1, 658.1 |

Here again, the influence of the cognate metal seems unmistakable and distinctive. My only explanation lies in the complexity of the base, although I admit that the evidence, so far, is not conclusive.

(*Abstract*)

STANDARD WAVE-LENGTHS FOR USE IN OPTICAL MEASUREMENTS

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The author raises the question as to the most suitable wave-lengths to select for use in optical measurements. The traditional series (the C, D, F and G lines in the spectra of sodium and hydrogen) is unsuitable for modern use, and has been abandoned by pioneer workers in all branches of optical science. The most suitable standards would include lines selected from the series—

Li 6708, Cd 6438, Na 5893, Hg 5461, Cd 5086, Cd 4800, Hg 4359. Of these lines, the most accessible at the present time are, Li 6708, Na 5893, Hg 5461, Hg 4359.

These seem to be the most likely to secure widespread acceptance as a substitute for the earlier series of standard wave-lengths. An expression of opinion by the members of the congress is invited.

(*Abstract*)

THE CHEMICAL PROPERTIES AND RELATIVE
ACTIVITIES OF THE RADIO-PRODUCTS
OF THORIUM

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1. Numerous Chemical reactions of the radioactive products of thorium were studied. It was found that each product has its own characteristic chemical properties. From a knowledge of these properties, methods were worked out for the separations of the various products from inactive substances and from one another and for the preparation of several of these products completely free from radio-active impurities.

2. The relative activities of thorium $B+C+D$ and thorium $X+Emanation+A$ was determined by preparing thorium X entirely free from $B+C+D$ and determining its change of activity with time. Knowing the periods of each of the substances, the activity of $B+C+D$ was found to be 0.427 of that of thorium $X+Emanation+A$.

3. By determining the initial activity of pure radiothorium and its change of activity with time, it was found that the products of radiothorium are 5.23 times as active as the radiothorium itself.

4. In order to make the calculations of the results of 3 and 4, it was necessary to know the periods of the various radio bodies accurately. As a result of new determinations, the accepted periods of thorium X and thorium B were confirmed as 3.64 days and 10.60 hours respectively. The period of thorium C was found to be 60.8 minutes instead of 60.4 minutes (Lerch).

5. It was shown that the accepted value of the range of thorium X cm, was incorrect and that the true value is 4.0 cm. This value is in good accord with that expected from the period of this substance.

6. As a result of Geiger's work it is shown that the total ionization of an alpha particle is proportional to the $2/3$ power of its range. It is then shown that the activities found in 3 and 4 are in excellent agreement with those expected from the ranges of the various active substances. As the result of this work, the uncertainty which has hitherto existed in regard to the thorium series is now removed.

ON THE CONDUCTIVITY AND IONIZATION OF
SODIUM ETHYLATE, POTASSIUM ETHYLATE,
LITHIUM ETHYLATE, SODIUM PHENOLATE,
POTASSIUM PHENOLATE, LITHIUM PHENO-
LATE, SODIUM PHENYLTHIOURAZOLE,
SODIUM IODIDE, SODIUM BROMIDE,
AND OF MIXTURES OF THESE ELEC-
TROLYTES, IN ABSOLUTE ETHYL
ALCOHOL AT 0°, 25° AND 35°

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The conductivities of the above named compounds have been measured in absolute ethyl alcohol at 0°, 25°, and 35° in concentrations varying from N/1 to N/256,000. The per cent of ionization is much lower in concentrated alcoholic solutions than in the corresponding aqueous solutions, the ionization of N/1 solutions of sodium ethylate and of sodium phenolate, for example, being 14.8 per cent and 12.2 per cent, respectively, at 25°. The decrease in ionization with rise in temperature is about 0.4–0.5 per cent per 1°. The maximum molecular conductivity is reached in concentrations between N/2000 and N/8000. As an example, we have found the molecular conductivities of N/1, N/2, N/4, N/8, N/16, N/32 and N/8000 solutions of sodium ethylate at 25° to be 4.93, 7.78, 10.37, 13.04, 15.98, 19.16, and 33.2, respectively.

UEBER DIE REAKTION ZWISCHEN OZON UND WASSERSTOFFPEROXYD

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Der Verlauf der Reaktion zwischen Ozon und Wasserstoffperoxyd, welcher als Umsetzung zwischen den typischen Vertretern der "Ozonide" und der "Antozonide" ein besonderes Interesse zukommt, wurde in Gemeinschaft mit Herrn Dr. A. Brugstaller näher untersucht.

Es handelte sich zunächst darum eine Methode zu finden, um die beiden Stoffe neben einander zu bestimmen. Denn die Bestimmung des einen allein würde unzureichend sein, da man von vornherein keine Sicherheit hat, in welchem stöchiometrischen Verhältnis die Umsetzung erfolgt; es hat sich auch im Verlauf der Untersuchung gezeigt, dass diese doppelte Bestimmung zum Verständnis des Vorganges unbedingt erforderlich ist.

Nach vielen Versuchen, auf welche hier nicht näher eingegangen werden kann, ergab sich dass man beide Substanzen neben einander recht genau auf jodometrischem Wege bestimmen kann, wenn man zunächst Bromkalium auf das Gemisch einwirken lässt, und dann Jodkalium zusetzt. Wenn die Lösung schwach sauer ist und die geeigneten Konzentrationen angewendet werden, so reagiert nur das Ozon, nicht aber das Wasserstoffperoxyd merklich mit dem Jod- und Bromkalium und es kann durch Titration des ausgeschiedenen Jods die Menge des Ozons ermittelt werden. Der Umweg über das Bromkalium ist deshalb notwendig, weil bekanntlich Ozon aus saurer Jodkaliumlösung mehr als die äquivalente Menge Jod frei macht, während bei dem Bromid diese Anomalie verschwindet. Hierauf setzt man eine grössere Menge Schwefelsäure und etwas Molybdänsäure hinzu, welche ein ausgezeichneter Katalysator für die Reaktion



ist, wodurch nach sehr kurzer Zeit eine der obigen Gleichung entsprechende Menge von Jod frei wird.

Sämtlich Versuche wurden bei 0° in $1\frac{1}{10}$ normaler Schwefelsäure ausgeführt. Unter diesen Umständen geht die Umsetzung so langsam vor sich, dass ihre Geschwindigkeit gut gemessen werden kann. Andererseits ist nach früher von uns ausgeführten Versuchen hier die freiwillige Zersetzung von gelöstem Ozon so langsam, dass nach etwa zwei Tagen erst ein Drittel des Ozons verschwunden ist. Man sollte demnach erwarten, dass die freiwillige Zersetzung des Ozons gegenüber der Reaktion mit dem Wasserstoffperoxyd, die schon nach weniger als einer Stunde zur Hälfte abgelaufen ist, vollkommen verschwindet.

In den folgenden Tabellen sind die Resultate der Versuche mitgeteilt. Die Zeit ist in Minuten, die Konzentrationen in Millimol im Liter angegeben.

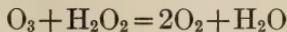
| | t | O ₃ | H ₂ O ₂ | K·10 ³ |
|------|----|----------------|-------------------------------|-------------------|
| I. | 0 | 1,08 | 1,69 | — |
| | 6 | 0,46 | 1,53 | 62 |
| | 13 | 0,25 | 1,44 | 49 |
| | 20 | 0,135 | 1,39 | 45 |
| | 29 | 0,70 | 1,32 | 41 |
| | 39 | 0,045 | 1,32 | 35 |
| II. | 0 | 1,50 | 0,78 | — |
| | 6 | 1,00 | 0,72 | 29 |
| | 14 | 0,51 | 0,66 | 33 |
| | 22 | 0,35 | 0,625 | 28 |
| | 30 | 0,205 | 0,595 | 29 |
| | 45 | 0,108 | 0,545 | 25 |
| III. | 0 | 1,77 | 0,400 | — |
| | 5 | 1,58 | 0,384 | 9,9 |
| | 14 | 1,32 | 0,372 | 9,1 |
| | 24 | 1,00 | 0,362 | 10,2 |
| | 39 | 0,63 | 0,330 | 11,5 |
| | 56 | 0,407 | 0,302 | 11,4 |

Bei der Betrachtung dieser Messungen fällt sofort auf, dass die Mengen von Ozon und Wasserstoffperoxyd, welche nach Ablauf einer gewissen Zeit verschwunden sind, durchaus nicht äquivalent sind, sondern dass stets sehr viel mehr Ozon verschwunden ist als Wasserstoffperoxyd.

In der folgenden Tabelle sind in der ersten Spalte die Konzentration des Ozons, in der zweiten diejenige des Wasserstoffperoxyds am Anfang des Versuches, in der dritten das Verhältnis der beiden α , in der vierten das Verhältnis der zersetzen Mengen beider Stoffe am Schluss des Versuches β_1 und in der letzten das Verhältnis β_2 , nachdem die Häfte des vorhandenen Ozons zersetzt war, angegeben. Die Zahlen sind aus den oben angegebenen Versuchsdaten berechnet mit Ausnahme der in der ersten Zeile angeführten. Bei diesem Versuch war infolge des grossen Ueberschusses an Wasserstoffperoxyd die Geschwindigkeit so gross, dass der zeitliche Verlauf der Reaktion nicht gemessen werden konnte, sondern nur das Verhältnis der beiden zersetzen Stoffe nach dem vollständigen Ablauf der Reaktion.

| O ₃ | H ₂ O ₂ | α | β_1 | β_2 |
|----------------|-------------------------------|----------|-----------|-----------|
| ca 1 | 30 | ca 0,03 | 1,08 | — |
| 1,08 | 1,69 | 0,64 | 2,8 | 3,9 |
| 1,50 | 0,78 | 1,93 | 5,8 | 7,9 |
| 1,77 | 0,40 | 4,42 | 14 | 18 |

Man sieht aus den Zahlen, dass nur bei dem ersten Versuch, bei dem der Ueberschuss des Wasserstoffperoxyds sehr gross war, annähernd gleich viele Moleküle beider Stoffe zersetzt werden, bei verdünnterem Peroxyd aber sehr viel mehr Ozon als dem Peroxyd äquivalent ist. Es kann dies natürlich nicht etwa dadurch erklärt werden, dass die Reaktion zwischen den beiden Stoffen nach einer anderen als der allgemein angenommenen Gleichung



verläuft, da das Verhältnis ganz veriaibel ist.

Es scheint ganz allgemein, dass man sich dem stöchiometrischen Verhältnis um so mehr nähert, je schneller die Reaktion abläuft. So fanden wir bei Versuchen in alkalischer Lösung 1,25 bis 1,33, und so erklärt sich auch das von Sir Henry Brodie gefundene Resultat, dass in alkalischer Lösung bei einem Ueberschuss von Peroxyd ebenfalls annähernd gleich viel Moleküle beider Stoffe zersetzt werden.

Aus diesen Beobachtungen ist zu schliessen, dass gleichzeitig mit der Reaktion mit dem Peroxyd auch noch eine spontane Zersetzung des Ozons stattfindet. Nun haben frühere Ver-

suche von Herrn Dr. Burgstaller und mir gezeigt, dass unter den angewendeten Versuchsbedingungen diese freiwillige Zersetzung so langsam stattfindet, dass sie während der kurzen Zeit der Versuche ganz unmerklich sein müsste. Es muss daher angenommen werden, dass die freiwillige Zersetzung des Ozons durch die Gegenwart von Wasserstoffperoxyd sehr stark beschleunigt wird.

Durch diese Annahme lässt sich auch eine Erscheinung verstehen, die sich bei den Versuchen über die freiwillige Zersetzung des Ozons wiederholt gezeigt hatte, ohne dass es damals gelang, eine Erklärung für dieselbe zu finden; wir fanden nämlich für die Geschwindigkeit dieser Zersetzung unter anscheinend ganz gleichen Bedingungen sehr verschiedene Werte. Es wurde damals vergeblich nach einem Katalysator gesucht, der eine so starke Wirksamkeit hätte, um diese Verschiedenheiten zu bewirken. Metallsalze und verschiedene andere Stoffe die wir untersuchten, zeigten keine oder keine hinreichend starke katalytische Wirksamkeit. Es scheint nun nach den angeführten Versuchen sehr wahrscheinlich, dass das Wasserstoffperoxyd der damals vergeblich gesuchte Katalysator ist. Freilich lässt sich das nicht direkt nachweisen, da es bei den früheren Versuchen niemals gelang, eine Spur von Wasserstoffperoxyd zu entdecken, bei der grossen Empfindlichkeit der Zersetzungsgeschwindigkeit des Ozons gegen geringe Spuren von Wasserstoffperoxyd können aber Mengen desselben, die weit unter der Grenze der analytischen Nachweisbarkeit liegen, noch von sehr erheblichem Einfluss auf die Reaktionsgeschwindigkeit sein.

Es geht dies sehr deutlich aus dem letzten des oben angeführten Versuche hervor. Hier tritt bei einer Konzentration des Wasserstoffperoxyds von 0,4 Millimol im Liter die Reaktion des Ozons mit demselben schon sehr stark zurück. Die Zeit, in welcher ein Drittel des vorhandenen Ozons zersetzt ist, ist nur der $\frac{1}{10}$ Teil der Zeit, welche zum gleichen Grade der Zersetzung bei Ozon allein erforderlich ist.

Wie die Spuren von Wasserstoffperoxyd bei den Versuchen mit Ozon allein entstanden sein mögen, lässt sich nicht mit Bestimmtheit sagen. Es kann sein, dass sich dasselbe im Ozonatator gebildet hat; denn wenn auch der Sauerstoff durch Phosphorpentoxyd getrocknet war, können doch minimale Mengen

von Wasser an den Glaswänden haften; es kann auch sein, dass es in nicht mehr nachweisbaren Mengen bei der Einwirkung von Ozon auf die verdünnte Schwefelsäure entsteht. In beiden Fällen wäre es leicht zu verstehen, weshalb auch bei anscheinend gleichen Versuchsbedingungen die Mengen nicht gleich sind.

Bei der nicht allzu grossen Genauigkeit der Messungen, die wegen der kurzen Zeiten und der geringen Konzentrationen unvermeidlich ist, kann man die Gleichungen, nach der die beiden Reaktionen verlaufen, nicht leicht mit einiger Sicherheit feststellen. Aber eine wichtige Konsequenz lässt sich aus den Versuchsdaten entnehmen: nämlich, dass die katalytische Wirksamkeit des Wasserstoffperoxyds auf die Zersetzung des Ozons langsamer mit seiner Konzentration wächst als die Geschwindigkeit, mit der es mit dem Ozon reagiert. Denn je konzentrierter das Wasserstoffperoxyd ist, um so mehr nähert sich das Verhältnis zwischen den beiden zersetzten Stoffen dem theoretischen Wert, bei sehr verdünntem Peroxyd dagegen ist die zersetzte Menge desselben nur ein kleiner Bruchteil der zersetzen Ozonmenge.

Hiermit steht auch die Tatsache im Einklang, dass bei sehr verdünntem Wasserstoffperoxyd, (Versuch II und III) die Konzentration des Ozons nach der Gleichung einer Reaktion erster Ordnung abnimmt. Hier ist eben fast nur die Zersetzung des Ozons merklich und die Menge des fast ausschliesslich als Katalysator wirksamen Peroxyds wenig veränderlich.

THE ELECTRICAL PRECIPITATION OF CARBON SMOKE

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SUMMARY

(1) The presence of a small amount of dirt lowers the critical voltage of corona formation, the corona appearing as bright scintillating points. The presence of a coating of soot upon the surface of the conductor affects the appearance of the corona but little.

(2) The electrical discharges take place in coal smoke in the same way as in air. The fibrous brush discharge characteristic of the positive corona is distinctly visible. The glow discharge is of a blue color. This is not due to absorption of violet light by the smoke, for a purplish glow loses none of its characteristic color when viewed through smoke.

(3) The presence of smoke causes an increase in the difference of potential between the inside corona wire and the outside cylinder while the ionization current is decreased. Schmidt has noted the same effect in the case of cement dust. This is due to the great decrease in the ionization of the flue gases due to the presence of smoke.

(4) Coal and oil smokes are precipitated in the same way as the various kinds of fumes. When precipitation is produced by a point discharge, a unidirectional current is much more effective than an alternating one. An alternating current produces a greater amount of precipitation when there are rapid oscillations produced in it by a series spark gap. This is due to the fact that the pressure of the electrical wind is very much greater from an electrode kept at a constant potential than from one charged from an induction coil or a transformer.

(5) Very little difference was obtained in the precipitation

of dense coal smoke in cylindrical pipes, between an alternating current and unidirectional current when a similar corona form of discharge was used. The precipitation seemed to be comparatively greater for a dense smoke than for light smoke. From this it would follow that dilution of the fume or smoke laden gases should be prevented as much as possible.

(6) Clearances of 90 and 95% have been obtained by passing extremely dense smoke through a corona discharge less than two feet in length. These experiments indicate that the greatest efficiency of precipitation can be obtained by keeping the suspended matter from being diluted and by exposing them as much as possible to the streams of ions flowing from the corona. This can best be obtained from objects placed near the collecting electrodes indicating that the matter being deposited moves in straight lines.

(7) Some kinds of smoke show selective precipitations, a thin cloud of white or bluish particles coming out from the corona discharge. Part of this is water vapor which may have condensed after the carbon and tarry matter had been precipitated. Whether this selective action is due to a difference in the size of the suspended particles or to a difference in their composition has not yet been determined.

(8) The hot gases as they leave the furnace contain a very great number of ions of comparatively great mobility and the ionization current due to these ions may be quite large. This current has been described in a previous part of this paper. The presence of smoke decreases the number and mobility of these ions very greatly, and hence decreases the current due to this cause. This effect is given in (3). Besides this ionization current there is the current due to the ions produced in the corona discharge itself. In the work on the electrification of dust and sprays, it was shown that these ionic currents charge the suspended particles. It is doubtful, however, if the presence of the particles causes any material decrease in the current due to these ionic streams.

(9) In the theory of the electrical wind it can be shown that the force due to ionic streams increases with the size of the particles. On the other hand, the force on a particle due to

the action of the electric field on its charge decreases with the size of the particle. For very fine particles, the latter force may be of importance, but for ordinary smoke and fine particles the force due to the ionic streams is probably the preponderating one.

(10) Precipitation of coal smoke was produced in a three inch cylinder (four feet in length) placed in a horizontal position. The active electrode consisted of a No. 28 steel wire. An alternating voltage was used. The cylinder was heated to redness on the under side by a row of Bunsen burners. Precipitation was then qualitatively just as complete, the soot being deposited upon the upper surface of the cylinder.

(11) The character of the corona discharge is probably very greatly affected by the resistance, inductance and capacity of the circuit. The writer hopes to investigate some of the effects produced by the constants of the circuit upon the nature of the ionic streams produced in the corona discharge.

(12) The application of electrical precipitation to the smoke problem has not as yet been tried on a commercial scale. Laboratory experiments indicate that the problem is essentially the same as that of the precipitation of fumes and dust. The use of cylindrical electrodes results in a much more uniform electrical discharge if the active electrode is made the axis of the cylinder. While the brush form of discharge from points is only a good precipitating agent when the current of gas is small, the corona discharge is effective for much greater velocities of the gas containing the suspended particles. Under these conditions the suspended particles need remain but a short time in the region where the corona discharge is taking place, so that the size of the precipitation chamber can be greatly reduced.

(*Abstract*)

THE PRESERVATION OF HYDROGEN PEROXIDE

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The object of this investigation was to study the speed of decomposition of hydrogen peroxide at 80° centigrade, and the influence of various catalysts, both positive and negative, upon the speed of decomposition of the peroxide.

At room temperature the course of the reaction may be followed by shaking the hydrogen peroxide solution in a flask placed in a constant temperature bath and measuring the volumes of the oxygen gas evolved in certain time intervals. At 80° C this method cannot be employed, for the agitation of the solution introduces a factor which makes it impossible to obtain concordant results. The method employed to find the rate at which the hydrogen peroxide was breaking up, was to titrate the solution with potassium permanganate in sulphuric acid solution.

In measuring this reaction the container used is of primary importance. Round bottomed Jena flasks, after weeks of consecutive steaming and treatment with hot concentrated hydrochloric acid, gave a minimum rate of decomposition of the hydrogen peroxide. Concordant results were obtained with different flasks, moreover experiments carried out on different days gave results well within the error of the experiment.

The rate of decomposition of hydrogen peroxide in quartz flasks is less than in the Jena flasks described above.

The purity of the water used to dilute the hydrogen peroxide solution was found to be of utmost importance. The conductivity water used was run direct to from the still in the reaction flasks. In several experiments water was used that had been collected and stored in Jena flasks at room temperature for two or three hours. It was found that even in this short time

enough impurity was dissolved from the glass to accelerate the decomposition of the hydrogen peroxide to a marked degree.

Solutions of sodium silicate, sodium carbonate and sodium hydroxide decompose hydrogen peroxide solutions. In equimolecular solutions the catalytic effect of these substances increases in the order given.

Calcium hydroxide does not act as a catalytic agent. A solution of hydrogen peroxide saturated with this substance at 80° decomposes at the normal rate.

A solution made by digesting ground glass with conductivity water was found to decompose hydrogen peroxide readily. This is probably caused primarily by metallic oxides held in a state of colloidal suspension, rather than to the presence in the solution of alkaline silicates and hydroxides.

Acetanilide acts as a negative catalyst toward hydrogen peroxide, even when only 0.00148 gram molecules per liter are present. It preserves solutions which contain positive catalysts such as sodium hydroxide, and the solution constituents of glass.

Concentrated solutions of sodium chloride preserve hydrogen peroxide. The addition of one gram molecule of sodium chloride per liter approximately doubles the time in which one-half of the solution will decompose. When sodium chloride is added to a solution of hydrogen peroxide which contains sodium hydroxide, the rate of decomposition is diminished to a slight extent only.

Sulphuric acid is a most efficient preservative for peroxide solutions; even when present in very small quantities 0.00066 gram of the acid per liter causes a measurable retarding of the reaction. The power of preserving increases with the concentration of the sulphuric acid, but no simple mathematical relation exists between the concentration of sulphuric acid and its retarding effect on the decomposition of hydrogen peroxide.

(*Abstract*)

THE IODINE COULOMETER AND THE VALUE OF
THE FARADAY

EDWARD W. WASHBURN AND STUART J. BATES

I

A critical examination of the most recent work with the silver coulometer indicates that the silver deposit obtained in it, even under the most favorable conditions, does not correspond exactly to the reaction, $\text{Ag}^+ + (-) = \text{Ag}$, but is larger than this reaction requires, probably by several hundredths of a per cent. Even when a correction is made for included material, which seems to be the principal source of error, there still remains a considerable degree of uncertainty as to the true electrochemical equivalent of silver; (1) because the exact correction which should be applied for the included material is difficult to determine and somewhat uncertain at best; and (2) because the influence of the oxygen of the air and the effect of filter paper, if it is used, both involve errors of uncertain magnitude; while if porous cups are employed, there is no proof of the absolute efficiency of their action.

While no other coulometer, hitherto investigated, has been found to have the high reproducibility of the silver coulometer under the most favorable conditions, the results obtained with the copper, the iodine, and the knall-gas coulometers, in so far as they are of value, all support the above conclusion that the deposit in the silver coulometer is too heavy.

II

Since the correct value of the faraday can only be obtained with certainty when the electrochemical reaction employed can be proved to be a perfectly clean cut one, free from all side reactions and preferably also from all other constant sources

of error which involve the application of "corrections," it is time that serious consideration be given to the problem of discovering a coulometer which will satisfy these requirements; for it is perfectly clear that the silver coulometer will never do so. With this object in mind, a thorough investigation of the iodine coulometer was undertaken. The investigation resulted in the perfection of a satisfactory instrument based upon the occurrence of the reaction, $3I^- = I_3^- + 2(-)$, at a platinum-iridium anode. A series of seven experiments to determine the reproducibility of the coulometer demonstrated that when the same current is passed through two coulometers in series, the amounts of iodine liberated at the two anodes show an average difference not greater than 0.002 per cent. which is within the limit of our experimental error.

In order to prove that the reaction is a perfectly clean cut one, free from interfering side reactions, the reversibility of the reaction was studied. In these experiments a platinum-iridium cathode surrounded by an accurately known quantity of a standard iodine solution was employed. If the reaction, $3I^- = I_3^- + 2(-)$, and the reverse one were the only ones which occurred at the electrodes, then the total amount of "free iodine" in the coulometer should be found unchanged after the electrolysis. In four experiments the amounts of "free iodine" in the coulometer, before and after the passage of 0.05 faraday, differed from each other by an average of less than 0.003 per cent. which is considerably less than the experimental error. In two of the experiments the small difference observed was positive and in the other two experiments negative, showing that it was due to accidental errors in the analysis and not to the presence of any side reaction. If additional evidence were required, the fact observed in two experiments, that a six-fold increase in current density at the anode had no appreciable effect upon the amount of iodine liberated, may be regarded as conclusive. The reaction in the iodine coulometer is, therefore, a perfectly clean cut one. The chief source of uncertainty in the silver coulometer, inclusion of solution by the deposit, is entirely absent from the iodine coulometer, since no deposit is obtained with the latter instrument.

III

It is the intention of the authors to attempt the determination of the value of the faraday with an accuracy of 0.005 per cent. by means of the iodine coulometer. In a few preliminary experiments in this direction, a comparison of the iodine coulometer with the silver coulometer of the form employed by Smith, Mather and Lowry in their absolute measurements gave a mean value of 96,540 coulombs for the faraday. The average deviation from the mean was 0.011 per cent. and the maximum 0.012 per cent.

This corresponds to an electrochemical equivalent of 1.1174 milligrams per coulomb for silver. This is 0.08 per cent. lower than the value obtained by Smith, Mather and Lowry and 0.05 per cent. lower than the recent value obtained by Rosa, Vinal and McDaniel at the Bureau of Standards. It confirms the conclusion that the deposit obtained in the silver coulometer does not correspond to the reaction, $\text{Ag}^+ + (-) = \text{Ag}$, and hence cannot be employed to determine the faraday. The four experiments upon which our preliminary value of 96,540 is based are perhaps too few to deserve very much weight, although we have no reason to believe that the above value is affected by any source of error amounting to 0.03 per cent. We think, however, that these experiments justify the conclusion that the value of the faraday is certainly *greater* than 96,500 coulombs per equivalent and that the *true* electrochemical equivalent of silver is certainly *less* than 1.11800 miligrams per coulomb.

BORON

An experimental lecture

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INTRODUCTION

It was thought that the members of the congress would be interested to hear about the properties of the element *Boron*.

A larger interest attaches itself to the elements than to the compounds. The differences and similarities between the elements are a constant source of speculation and the more we know about the different elements—all the elements, the more likely are we to find what is common, to find unity.

To the practical man the elements have still another interest. They may have some unusual properties capable of technical application. We would all like to know the properties of such elements as uranium, titanium, and a number of others, and to know what they are *good* for and it is the purpose of this lecture to introduce to you an element which has been for a long time a stranger—the element boron.

The element boron, I feel certain, you will find interesting from both points of view. It has exceptional characteristics—characteristics almost unique among elements and it is also capable of practical uses of considerable importance.

Three years ago I have published in the *Transactions of the American Electrochemical Society* an article in which the methods for the isolation of the element boron and the main properties of the element were described. The work has been going on steadily since then, mainly in the direction of developing the practical applications.

SPECIFIC RESISTANCE OF BORON

Among the characteristics of boron the most interesting are those pertaining to its electrical resistance.

The specific resistance of pure fused boron at ordinary temperature is high, very high, as compared to that of other elements which have any appreciable conductivity at all. Thus a piece of boron, regular in shape, two one-hundredths of a centimeter long and two one-hundredths of a centimeter square in cross-section has a resistance at 0°C of nearly two and a half million ohms. If you compare the resistivity of boron with that of other elements, to get an idea of its magnitude, you will find that the resistivity of boron is 10^{12} larger than that of copper at ordinary temperatures and that the element silicon, which comes next to boron in resistivity is still separated by a very considerable gap from it. The specific conductivity of boron at 0° is equal to about $0.5 - 0.6 \times 10^{-6}$ reciprocal ohms per cm/cm², the conductivity of silicon is 1.8, or nearly a million times as large as that of boron.

NEGATIVE TEMPERATURE COEFFICIENT OF RESISTANCE

This high specific resistance of boron is accompanied by a negative temperature coefficient of resistance, which is also unprecedented among elements. The resistance of boron drops very markedly as the temperature is increased, and it does this with exceptional rapidity at ordinary room temperature. At this temperature the conductivity of boron doubles in value for every seventeen degrees centigrade.

The little table gives measurements made on a very small piece of boron.

| Temperature | Resistance |
|-------------|--------------|
| 27°C | 775,000 ohms |
| 100 | 66,000 |
| 170 | 7,700 |
| 180 | 180 |
| 520 | 7 |
| 600 | 4 |

At temperatures above 1000° the resistance was but a fractional part of an ohm.

A comparison of this behavior of boron with that of other materials is instructive.

You all know that metals have a *positive* temperature coefficient of resistance; in other words, their resistance increases with temperature.

The metalloids have a negative temperature coefficient of resistance. Carbon in its amorphous form has a slight negative temperature coefficient, its resistance dropping in the ratio of two to one between ordinary temperature and white heat.

Silicon again comes nearest to boron but the gap separating the two is again very considerable. I do not know of any measurements made on specimens of chemically pure silicon. It is also difficult to make consistent measurements on silicon on account of its tendency to crystallize in grains of different size and shape, but some specimens of silicon will show a drop of resistance as large as one hundred to one between ordinary temperature and the temperature near its melting point, which is about 1400°C. Roughly speaking, therefore, between 0° and a good red heat the resistance ratio is for carbon, two to one, for silicon, one hundred to one, and for boron 10^6 to 10^7 .

Among *compounds* we find a large number with a negative temperature coefficient of resistance. You all are acquainted with the Nernst Glower which is a mixture of oxides and shows a very great drop in resistance with rise of temperature, which drop, however, begins or at least becomes measurable only at high temperatures, 500 to 600°C. The same holds true for pure oxides.

The drop of resistance of calcium oxide and of copper oxide from measurements made by Horton are given in the following tables.

| | Temperature | Resistance |
|---------------|-------------|-----------------|
| Calcium Oxide | 763° | 7×10^6 |
| | 1011 | 2×10^6 |
| | 1468 | 91 |
| Copper Oxide | 12° | 462,400 |
| | 59 | 91,560 |
| | 134 | 12,360 |
| | 1038 | 0.02 |

While calcium oxide shows a drop of resistance only at high

temperatures copper oxide shows a rapid drop of resistance around room temperature and in this way is very much similar to boron.

We get, therefore, the result that the element boron approaches in its electrical behavior more nearly certain compounds than the elements. I had occasion to point out in another place that it is the magnitude of resistance that determines the sign and value of the temperature coefficient of resistance and that no fundamental difference exists in that respect between elements and composite substances.

I have with me a few slides which represent graphically the change of resistance of boron with the temperature.

In Figure 1 the temperature interval is 27°—450°C. The change in resistance is so great that it is difficult to represent the measurements on one curve, so two curves are used. In the first one the temperature interval is 27°—200°C and the unit of resistance is a megohm; in the second one the temperature interval is 200°—450°C, the unit of resistance is 500 ohms. You see the piece had a resistance of 4 megohms at room temperature and of only a very few ohms at 450°.

In Figure 2, resistance measurements of another smaller piece of boron are reproduced and three ordinate scales are used, the resistance units being 10,000, 1,000, and 50 ohms respectively, the total temperature interval is room temperature to 650°C.

The cold resistance is 9,000,000 ohms; the resistance at 650° is too small to be represented even on the smaller scale of the last curve.

The relation between temperature and resistance is not a simple one but for small intervals of temperature one can assume that the drop in resistance is proportional to the resistance and the change in temperature, that is

$$\Delta R = -\propto R \Delta T$$

At ordinary temperature the temperature interval for which the resistance drops to half value is, as I said above, about 17°; this interval of temperature increases as the temperature rises, and at 600° it is about 80°.

This leads to an exponential expression for the resistance which can be used for small intervals of temperature of say 50° with only a small error.

The curve which I throw now on the screen shows the connection between the resistance of boron and the watt input. (Fig. 3) This curve has not the theoretical importance of the temperature-resistance curve but is useful in connection with practical applications. The general course of the curve is the same as that of the temperature-resistance curve. The drop of resistance with watt input is so rapid that it is hard to represent it on one scale even with such a small variation of wattage as is embraced by the curve, namely, between 7 and 28 watts. The curve refers to a small piece of boron in air.

So much about the electrical characteristics of boron.

INFLUENCE OF DISSOLVED ELEMENTS

The influence of addition of other elements dissolved in boron is no less interesting. This influence is of extraordinary magnitude so that even as small an amount as 0.1% of carbon, for instance, will increase the conductivity of boron manifold. When 7-8% of carbon are dissolved in boron the remarkable characteristics of boron disappear altogether and the material has a conductivity comparable to that of silicon or even carbon. The law of variation of the conductivity of boron with the content of dissolved material I have not established but the experiments as far as they have been carried out point to an exponential curve. These experiments are just as difficult as they would be interesting. One of the difficulties is the necessity of very accurate chemical analysis as a small error in the analysis would produce an enormous change in the curve.

It is again interesting to compare this behavior with that observed in other substances.

With metals the opposite is true; if one metal is dissolved in another the resistivity increases, not the conductivity. Silver is a better conductor than copper but addition of silver to copper increases the resistivity of the latter.

With "poor" conductors, however, the conductivity of mixtures is greater than that of pure substances. This general behavior of poor conductors has been pointed out by me previously.

Hand in hand with this diminution of resistivity goes the

decrease of the value of the temperature coefficient of resistance. The temperature coefficient of resistance of solutions of elements in boron is still negative but less so; so that while the difference in specific resistance at ordinary temperature between boron and its solutions is very great, this difference gets less and less as the temperature increases. Finally, at high temperatures, say 1000°, there is very little difference in the conductivity of boron and the conductivity of dilute solutions of other elements in boron; all the resistance-temperature curves seem to come together at high temperatures.

The reverse phenomenon has been observed with metals, but leading to the same final result. A solution of silver in copper is a poorer conductor than copper but the temperature coefficient of resistance which is positive in this case is smaller than that of copper. At high temperatures the two curves will probably come very near together.

The rise in resistance which takes place with good conductors, the drop in resistance which takes place in poor conductors, the above-described connection between the temperature coefficient and the magnitude of resistance all suggest the possibility that at a certain very high temperature all materials if preserved in solid or liquid form would show the same conductivity. What the value of that temperature is and what the theoretical significance of it may be are questions which I will not discuss here.

For the practical use of boron this influence of dissolved substances is very important, because one has it in his hand to change the specific resistance within very wide limits and also to change the temperature coefficient from the enormous value it has in boron to any desired value.

VOLT-AMPERE CURVE AND BREAKDOWN VOLTAGE

In order to follow the experimental demonstration of the properties of boron that I have in view, it is of importance to thoroughly understand the nature of the curve connecting the current and voltage across a piece of boron. The volt-ampere curves of solids have not been used very much in theoretical discussion, for the reason that they have not the fundamental

importance of the temperature resistance curve. The temperature-resistance curve is perfectly definite; the volt-ampere curve will vary with the way in which the heat is dissipated. This because a certain volt-ampere product means a certain watt input which may give any temperature according to conditions. These curves have, however, been used in the study of gaseous discharges to a great extent (Kaufman) for the simple reason that in this case volt-ampere curve is the only thing that can be easily determined.

In the study of the volt-ampere curve of solids or liquids three cases can be distinguished. (See Fig. 4) If the resistance does not vary with the temperature, then the volt-ampere curve is a straight line and $\text{tg}\alpha$ is a measure of the resistance (Curve I).

For a material with a positive temperature coefficient of resistance (metals, etc.) the curve will be convex to the axis of abscissae (Curve II); in some cases when the temperature coefficient is large enough a part of the curve may run almost parallel to the axis of ordinates (Curve III). In other words, there may be a region in which a very large variation in volts corresponds to a very small variation in current. This case is exemplified by iron, within a certain narrow interval, and also by tungsten. Placing these materials in hydrogen is favorable to this result, as the heat dissipation (conduction) at lower temperature is relatively more favored than at high temperatures (mostly radiation).

For a material with a negative temperature coefficient the general form of the volt-ampere curve is represented by Curve IV. The resistance corresponding to 0 current is represented by the tangent of the angle β and the whole curve will lie between this tangent and the axis of abscissae. This because the volts rise more slowly than if the resistance remained constant.

A few simple considerations will show that the curve will in general possess a *maximum*. From $E = RI$ it follows that

$$dE = R dI - I [dR]$$

I write the minus sign and understand by $[dR]$ the absolute value of the resistance change. For $I = 0$ we have, of course

$$\frac{dE}{dI} = R$$

For low values of current dE is represented essentially by RdI which is *positive*; therefore, the voltage first increases with the current. However, as the current increases the second factor $I[dR]$ becomes more and more important; since the first factor containing R becomes smaller because the resistance drops, we finally reach a point where the two are equal. At this point $dE = 0$ and the voltage is a maximum. From this point on $I[dR]$ will predominate and the volts will drop with increasing current. The general form of the curve is, therefore, that given by IV. It is seen that for the same value of voltage there correspond in general two values of current and that the curve consists essentially of two different parts, a rising part in which the conditions correspond to stability and a drooping part which is essentially unstable. On this drooping part no equilibrium is possible (unless there is external resistance in the circuit with a constant or rising characteristic). On constant voltage the current and the energy input (represented by the area of the curve) would increase until a condition equivalent to a short-circuit would take place.

The point M which separates the two branches of the curve and which corresponds to the maximum voltage possible across the resistor will, on this account, be called the "*breakdown*" voltage.

It is at first sight somewhat difficult to see why the breakdown does not occur with ever so small a voltage since the energy introduced into the resistor should cause a drop in resistance, this in its turn cause an increased energy input, and so on. It will, therefore, be instructive to derive the existence of a breakdown point on the basis of energy relations. I will consider only the very simple case in which constant voltage is applied, E . The energy input is equal to

$$W = \frac{E^2}{R}$$

and assuming that R is an exponential function of the temperature we get for the energy input the value

$$W = \frac{1}{c} E^{12} e^{\alpha T}$$

Let us assume that the temperature at which the breakdown occurs is low (This is true of boron). In this case we may assume that the dissipation of energy takes place only by heat conduction and therefore is proportional to the temperature difference and is equal to AT . In equilibrium energy input and output must be equal. We get the equation $\frac{E^2}{C} e^{-\frac{T}{C}} = AT$. By a simple reasoning it is easy to see that this equality is possible only when E is below a certain critical value. When the volts exceed this critical value the equality is no longer possible at any temperature and the input will always be larger than the output. This particular voltage will correspond to the breakdown voltage.

If the breakdown occurred at higher temperatures, the second part of the equation would contain a term corresponding to radiation but the general conclusion would not be changed. Nor will it be materially affected if the resistance-temperature function is not exactly exponential.

The form of the curve discussed up to the present is characteristic of boron itself and all similar materials which have a very large negative coefficient of resistance. According to the value of this temperature coefficient and also to the values of the constants C and A (nature of the surface, degree of heat insulation) the curve may assume different forms. After the maximum voltage corresponding to M is reached the voltage may drop only very slightly or move along a horizontal part giving a constant voltage with varying current (Curve V) and finally the maximum voltage may lie at very high temperatures so that the drooping part of the curve is not reached at all in ordinary work. In this case the curve is constantly rising, always remaining concave toward the X axis. The same form of volt-ampere curve may be obtained by combining a resistor with a positive temperature coefficient and one with a negative temperature coefficient of resistance, in series or in multiple.

These theoretical conclusions I am going to illustrate now with some slides I will project on the screen. They are the result of actual measurements made on boron and on boron with a small percentage of carbon.

Figure 5 gives a volt-ampere curve obtained from measure-

ments on a small piece of pure boron in air. The contacts were made by fusing on platinum wires. You see that the first part from 0 up to the maximum rises very rapidly. The tangent of the angle this part forms with the axis of abscissae, gives the resistance of the material at room temperature. At 400 volts the breakdown voltage is reached. The current value corresponding to this part is only about 0.004 of an ampere. After the breakdown had occurred the current rises and the voltage drops very rapidly.

On the next slide (Figure 6) the same measurements are represented but the part of the curve around the breakdown point is shown on a different scale.

The next slide (Figure 7) shows the volt-ampere curve of boron containing a small percentage of carbon. The breakdown voltage is lower, only about 80 volts in this particular case, but the general course of the curve is the same, except that the whole curve is lower.

Figure 8 shows the *time interval* which it takes the material to break down at different impressed voltages. You see that with the particular piece the breakdown voltage is about 85. As the voltage is gradually raised above this value the material breaks down in a time which is the smaller the higher the voltage applied, until at 140 volts the breakdown is practically instantaneous.

EXPERIMENTS DEMONSTRATING BREAKDOWN VOLTAGES

After these preliminary explanations I believe you will have no difficulty in following the experiments I am going to perform.

The first experiment intends to show the existence of the breakdown voltage. (Referring to blackboard) The connections are illustrated in Figure 9. A 110 volt circuit is used and by means of a potentiometer variable voltages can be applied to the system. Two 65 volt, 25 watt lamps are placed in series and one lamp, 65 volts, 15 watts, is placed in shunt with the boron piece. So long as the applied voltage is below the breakdown voltage of the boron piece, the voltage across the boron will be high and the lamp in shunt will be bright while the lamps

in series with the boron will be dark. When, however, the voltage applied to the boron will equal or exceed the breakdown voltage the resistance of the boron will drop rapidly, the lamp in shunt with the boron will become dark while the large current flowing through the boron and the lamps in series will make the latter glow with their normal brilliancy.

To get a low enough breakdown voltage in order to be able to carry out the experiment on a 110 volt circuit, I use in this experiment a piece of impure boron containing some carbon. I first apply 12 volts. (Making experiment.) Practically the total voltage is across the boron; the lamp in shunt is bright (although, of course, not up to normal brilliancy) but the lamps in series are perfectly dark. I increase the voltage to about 18. The lamps in series remain dark and the lamp in shunt becomes brighter. The boron had not broken down. Now I apply 70 volts, which is away beyond the breakdown voltage which is for this piece in the neighborhood of 40 volts. For a few moments the lamp in shunt is very bright since there are almost 70 volts across it which is above its rated voltage. But you see now that the same shunt lamp has become suddenly dull while the lamps in series become very bright. The boron has broken down and the voltage across it has dropped to but a very few volts. (Applause.)

In the next experiment I will proceed more slowly so as to determine the breakdown voltage more or less accurately. I shall probably find the breakdown voltage a little lower than that obtained by me in Lyon because the temperature today is higher than when I made the test. We all feel the heat. I am sure this boron piece is more affected by it than any of us. Its conductivity is probably increased 50 or 75%.

I apply 12 volts. At this voltage we might wait any length of time. The boron piece will never break down. The next step is 18 volts. The breakdown does not take place. I go to 28 volts and wait a couple of minutes. You see nothing happens. I now apply 40 volts.

I think at this voltage the piece will break down in three or four minutes. While waiting we may all try and picture to ourselves what is going on in this piece that transforms it from

a poor to a good conductor. According to the current ideas you will have to picture to yourself the atom of boron dissociating and throwing off electrons in a number which grows rapidly with the temperature.

You see the boron piece breaking down, the lamp in shunt becomes dull, the lamps in series bright. (Applause.)

In the next experiment I will show you the effect of temperature on the breakdown of pure boron. In order to get a low breakdown voltage with pure boron a very small thickness of it must be used. It is obtained by depositing a very thin layer of boron on a thin carbon filament; however, with the particular rod I am using now, about one-sixty-fourth of an inch thick, the breakdown voltage will still be above the 110 volts at my disposal and what I will demonstrate to you is this; I will apply 70 volts to it. The boron piece will not break down. I will approach a match to it and heat it very slightly, and the piece will break down. What you will see will be the same as before. The shunt lamp which is bright at first will become dark; the lamps in series, dark at first, will get bright. But you will also see that the boron will get incandescent, because the current and the energy are increased. We have waited now some time to be sure that 70 volts will not break down the rod; now please watch carefully both the boron and the lamps while I apply a match. You see that what I described above happens.

So much for demonstrating the breakdown voltage of boron. Now this is not only an interesting laboratory experiment, but it can be used in a practical way. Boron materials make an excellent "cut-out," that is, an element in electric circuits which will break down and open a path for current when the voltage has gone beyond a certain value.

EXPERIMENTS TO DEMONSTRATE VOLTAGE REGULATION

The following experiments will now demonstrate to you the possibility of obtaining by means of boron constant voltage with variable current (within certain limits). The variation of current usually occurs through a variation in the impressed voltage of the circuit, which variation may be due to a number

of causes, such as the variation of *speed* of electrical machinery. In every case a little boron regulator would preserve constancy of current through the protected circuit in spite of the fluctuations.

For all such applications the variation in the resistance of the boron regulator must be rapid, and, therefore, the boron must be prepared in the form of a filament of very small heat capacity and also conditions must be such that the heat dissipation is favored as much as possible.

The experimental arrangement I have here includes a boron regulator, a 65 volt, 15 watt lamp in shunt with the regulator and a 40 volt, 80 watt head-light lamp in series with it. As soon as we get to the point where the voltage across the boron regulator remains constant, taking out resistance and increasing the current will make the lamp in series get brighter and brightened but the lamp in shunt will stay at the same brightness. The constant voltage for this particular regulator is about 65 volts.

On reducing the resistance in series, the current increases but the total current is taken up by the boron regulator. The current through the shunt lamp remains constant since the voltage across it remains constant.

You see how little the lamp in shunt has varied in brilliancy while the lamp in series came up from dullness to full intensity. (Applause.)

In the next experiment the connections are the same but the boron filament used has a drooping characteristic. Beginning with a certain current the voltage diminishes as the current increases. As I turn out resistance you will notice that while the lamp in series grows brighter the lamp in shunt grows duller.

OTHER PROPERTIES OF BORON

I pass now to properties of boron other than electrical.

Boron is very hard. That could be expected. We knew that boron carbide is a very hard material. But boron itself is not only hard, boron and boron in which small percentage of other elements are dissolved can also be prepared in a form in which they are also tough to a certain extent, and in that way they differ from carborundum and other artificial hard materials.

The combination of these properties make possible their use for small bearings, such as meter jewels and for similar applications. It was, however, necessary to develop methods which would make a perfectly *homogeneous* material devoid of porosity and capable of taking a perfect polish.

These methods have now been developed and meter jewels were obtained, a large percentage of which were equal to diamond as to life and as to constancy of friction.

CAST COPPER

The list of practical applications of boron would be incomplete if I did not mention the use of boron sub-oxide, a by-product obtained in the manufacture of boron, for obtaining high conductivity cast copper.

This is an application which was not thought of when the substance was first prepared. Copper cast without additions is full of pores and blow-holes, therefore, mechanically unfit and of very low electric conductivity; the removal of the gases from copper by the known deoxidizers is liable to give an alloy containing a small amount of deoxidizer, an amount sufficient, however, to lower the conductivity of the copper to a large extent.

Boron sub-oxide, however, has the property of deoxidizing copper without combining with it, as boron sub-oxide has no affinity for copper. Tons of copper are cast now by this process, improving the quality of the product and cheapening it.

SPECTRUM

I will conclude this part of my lecture by showing you the spectrum of pure boron taken by no less an authority than Prof. Crookes. While we have gained in other directions, when we come to the spectrum we have lost. The spectrum of boron was supposed to contain about eighteen lines, the pure elementary boron gives only three lines. This shows the very great simplicity in the structure of boron, especially if you compare it with titanium or iron.

Temperature-Resistance Curve
Fused Boron

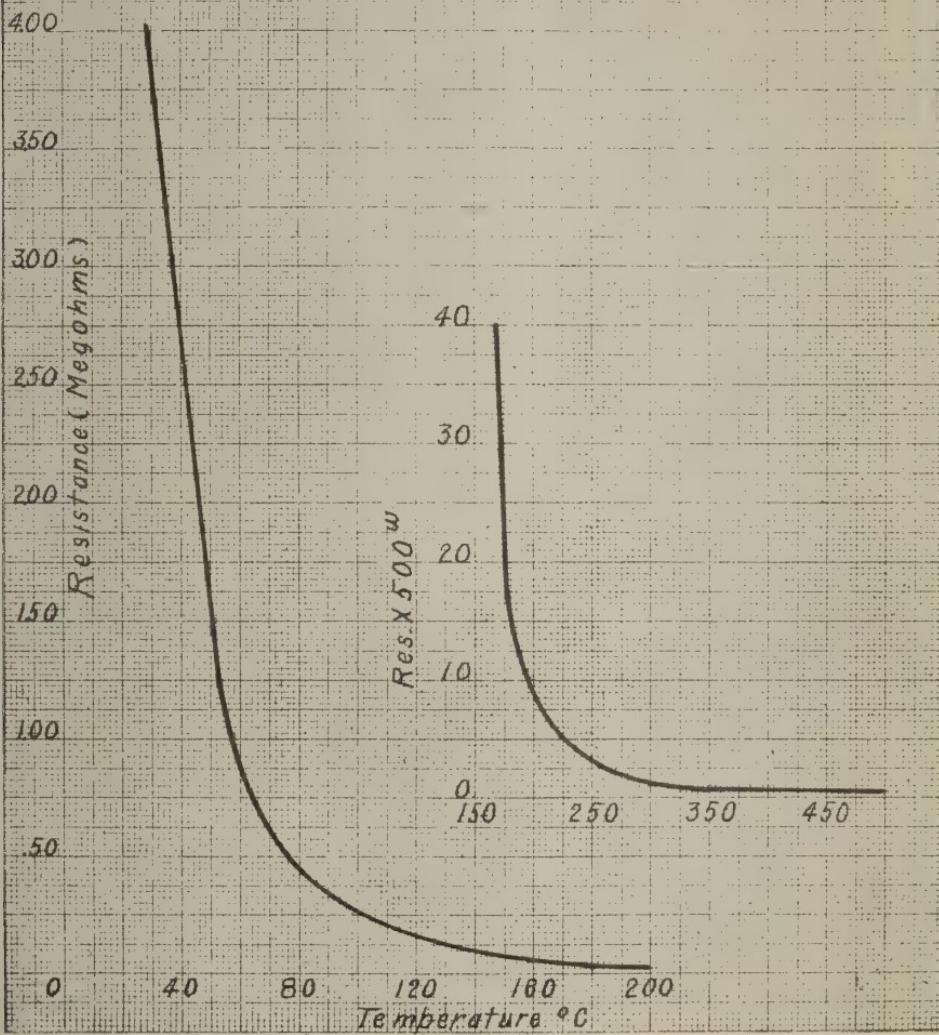


Fig. 1

Temperature-Resistance Curve

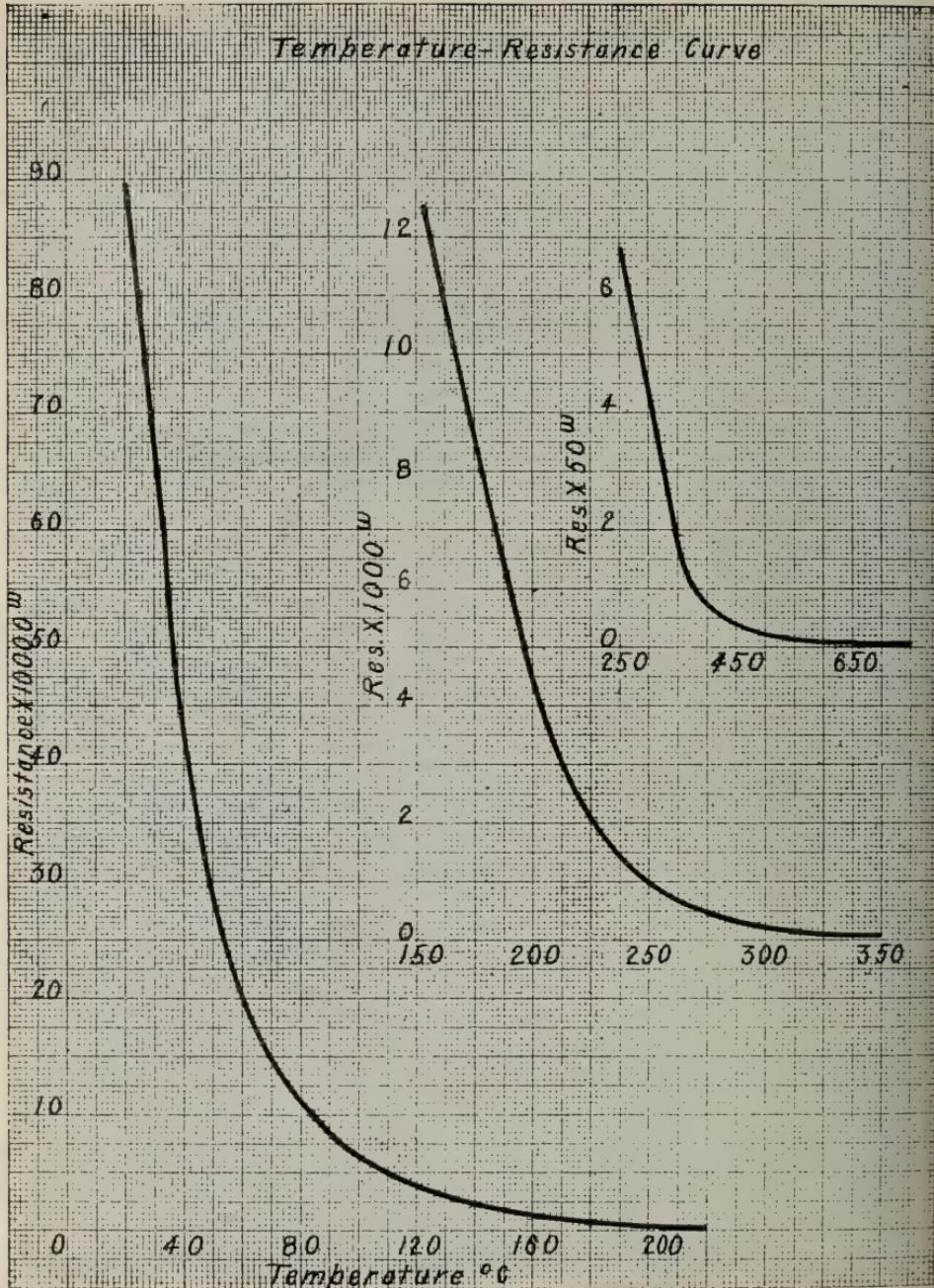


Fig. 2

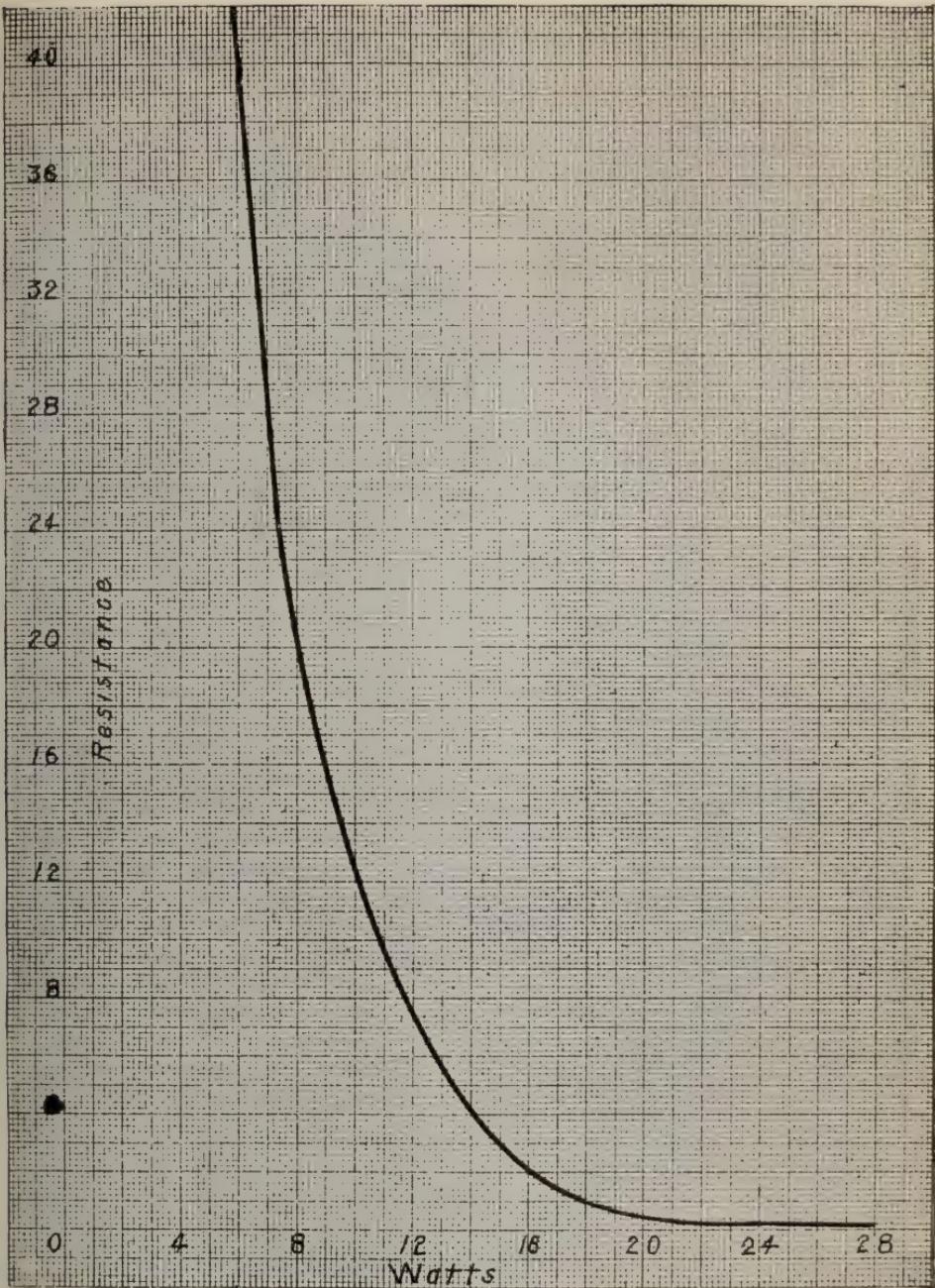


Fig. 3

Volt-Ampere Curve
of
Fused Boron
in AIR

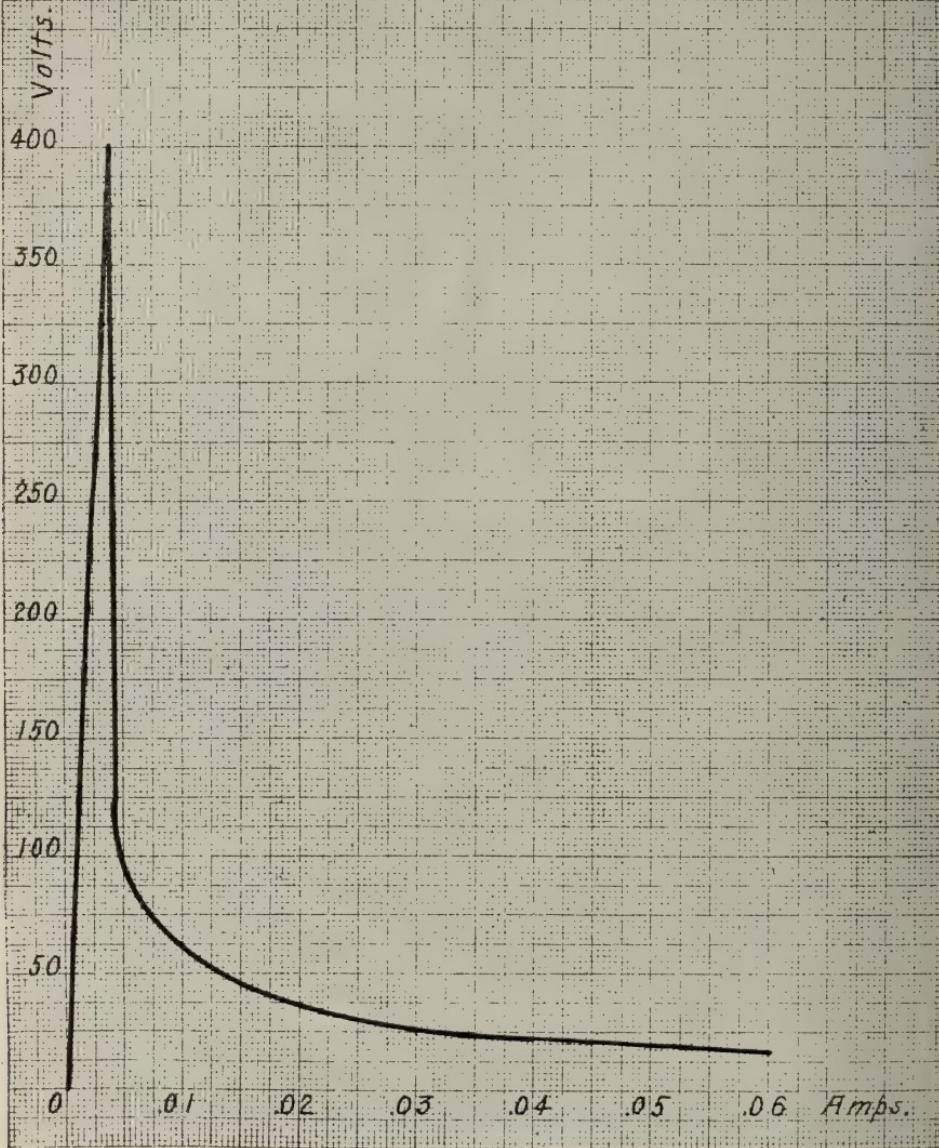


Fig. 5

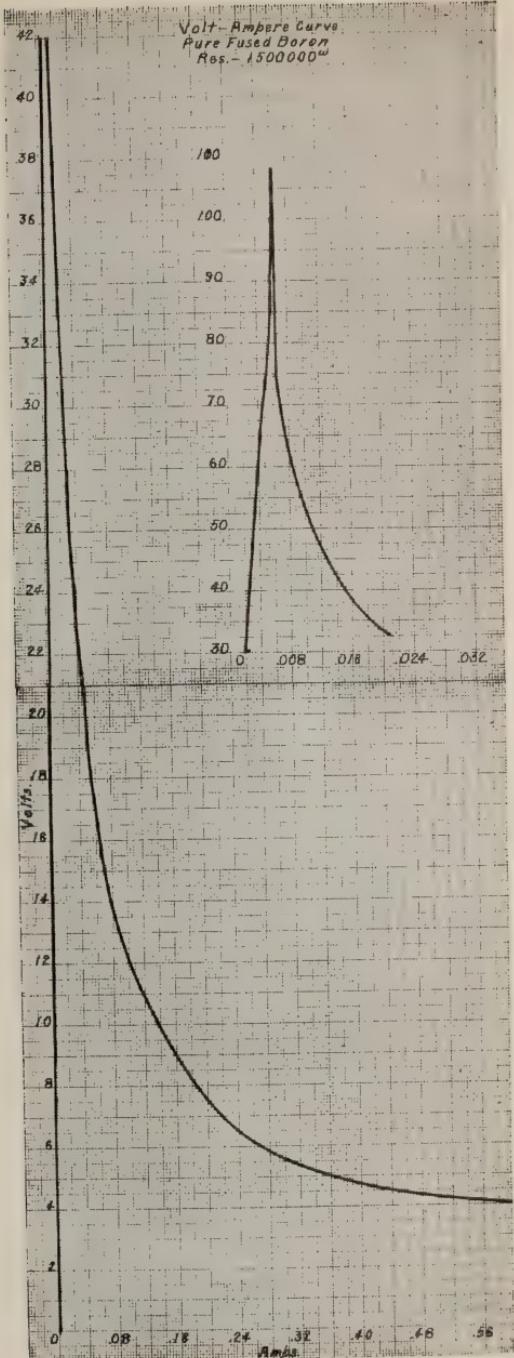


Fig. 6

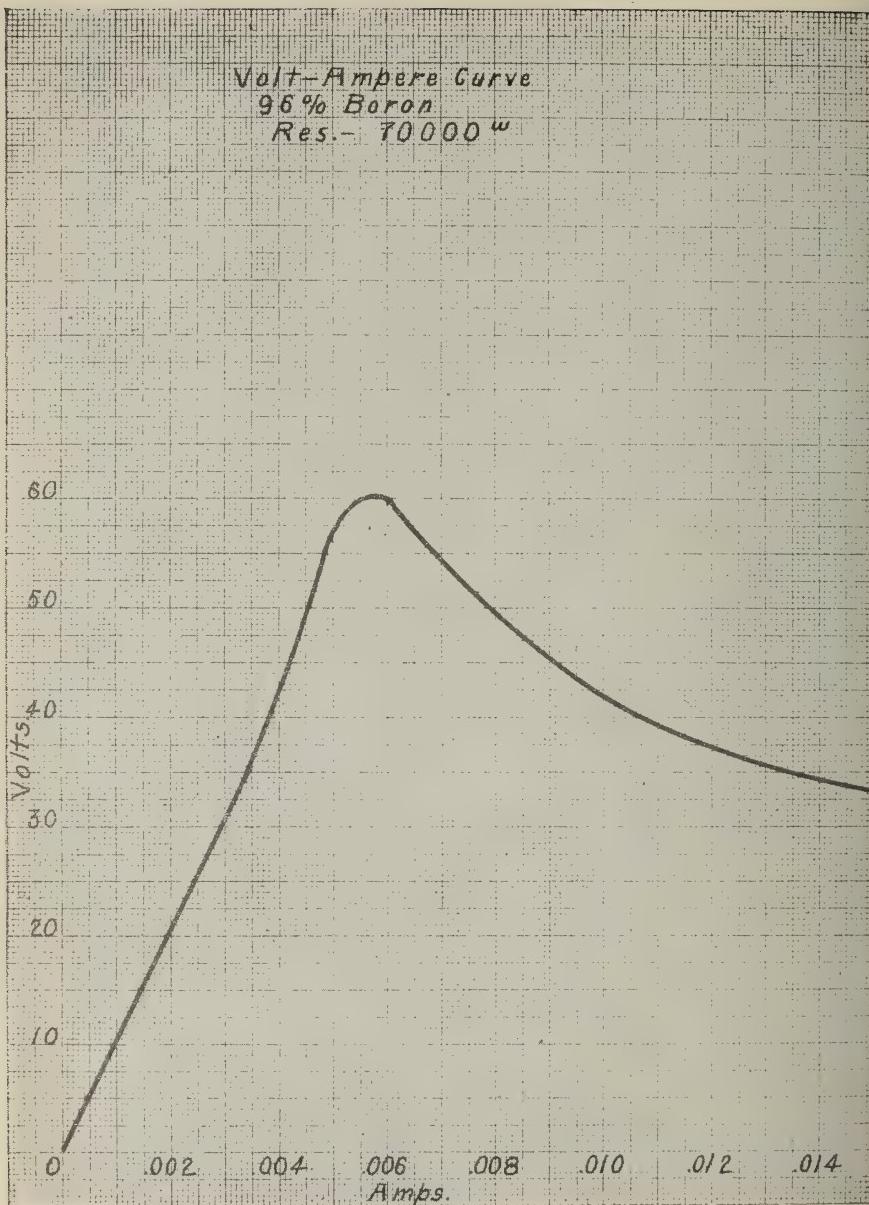


Fig. 7

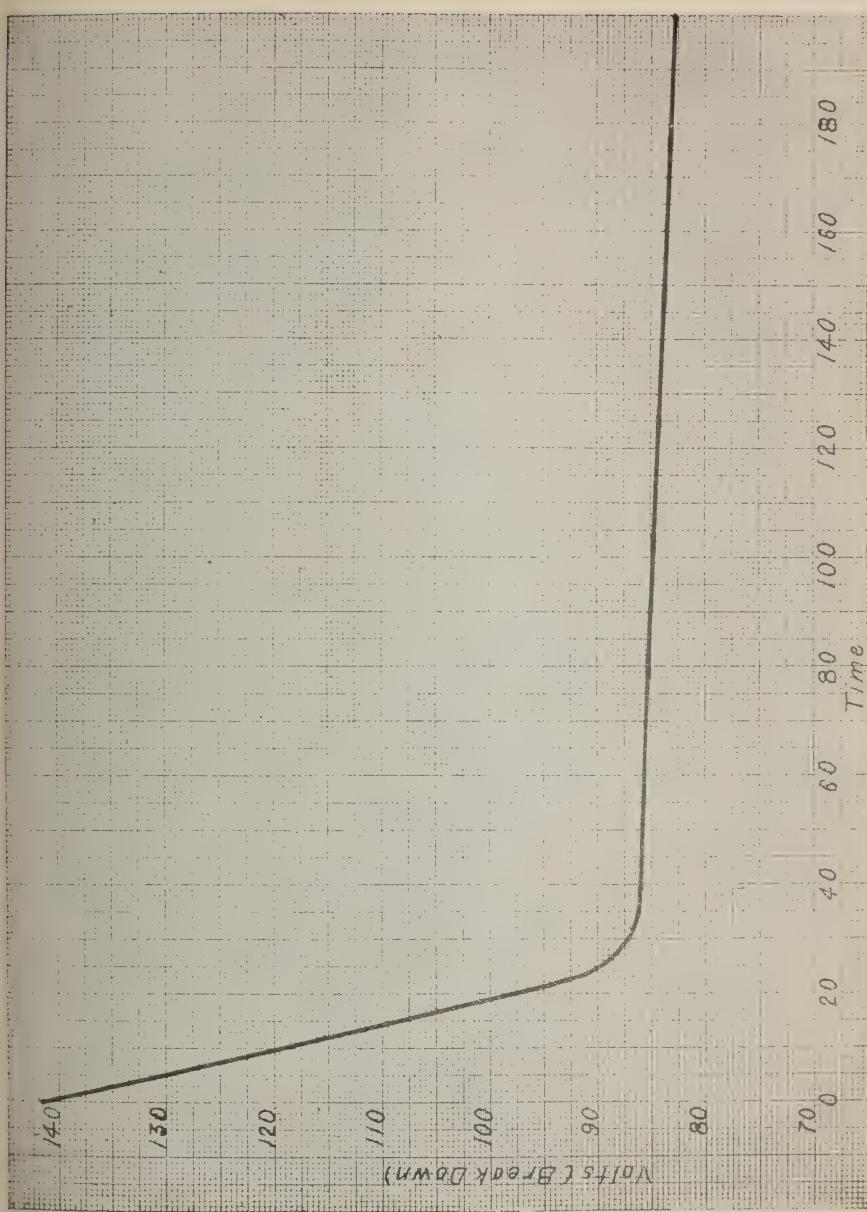


Fig. 8

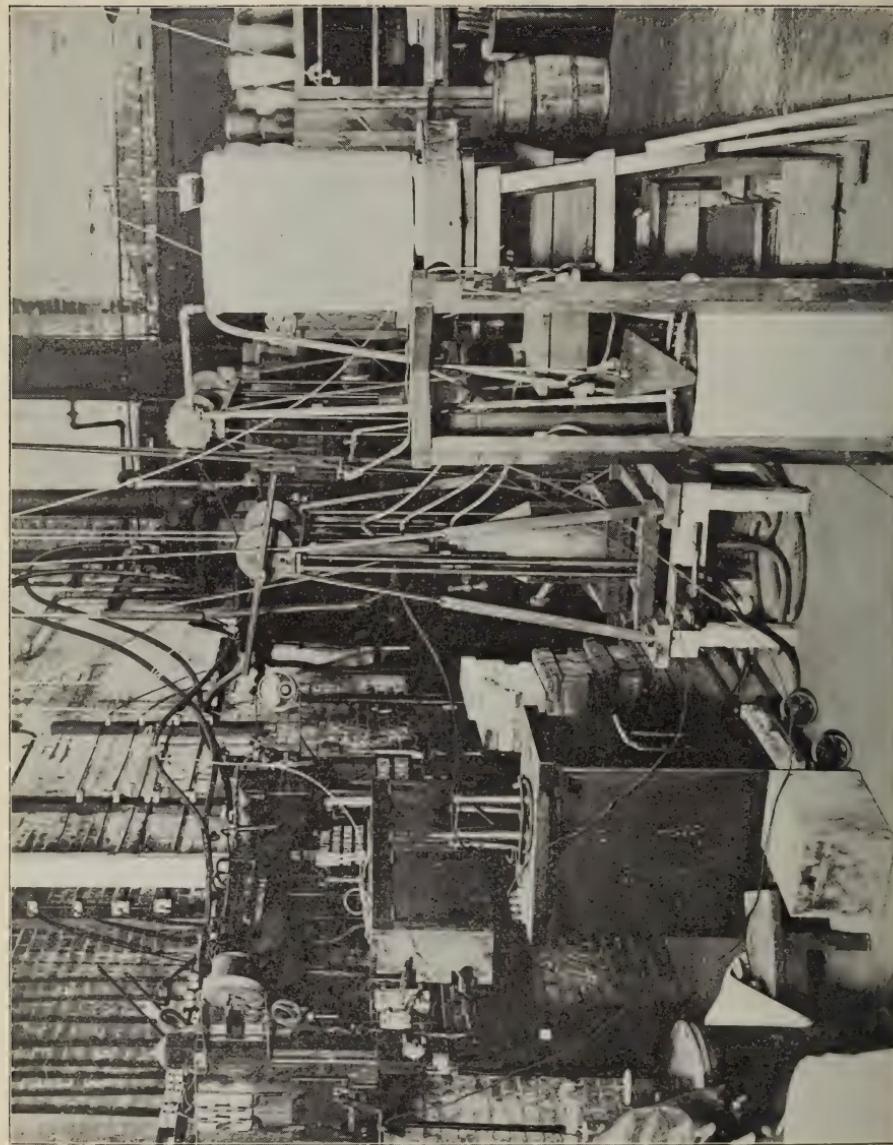


Fig. 11

Fig. 12

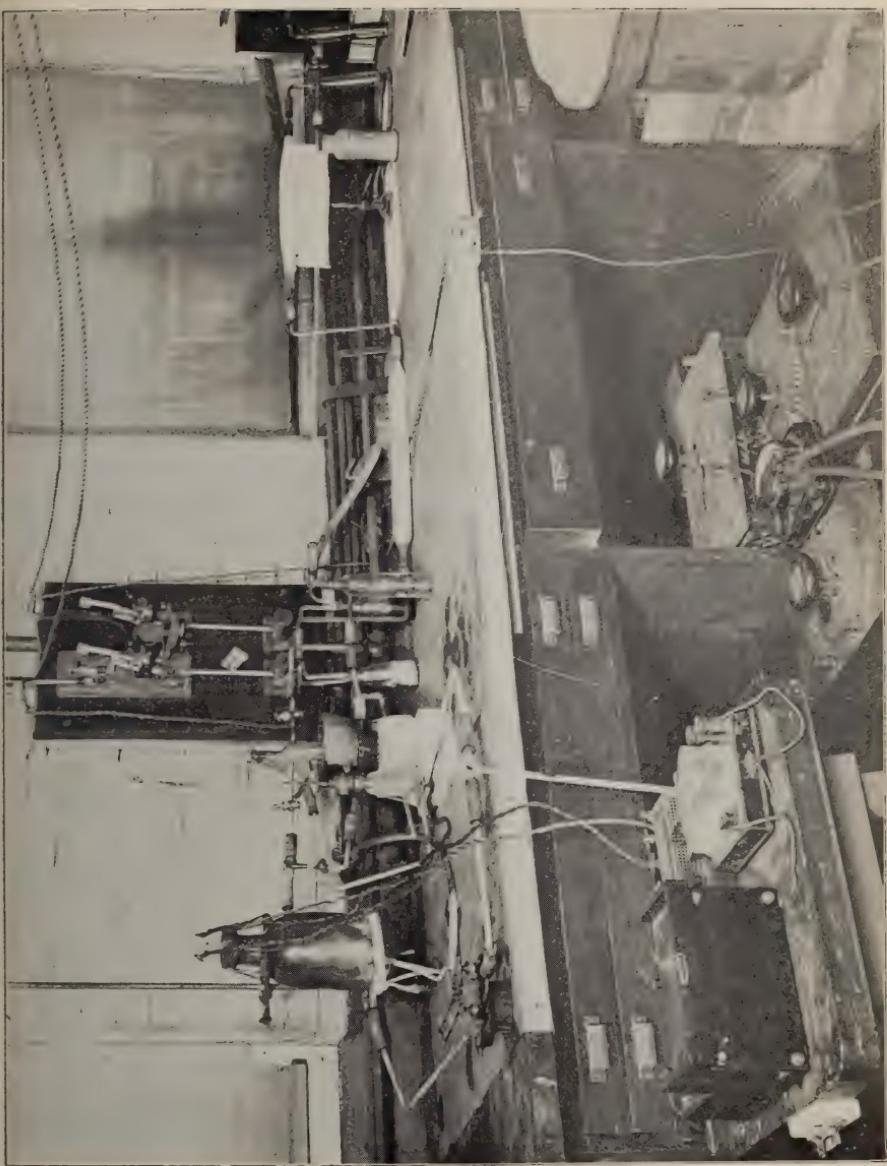
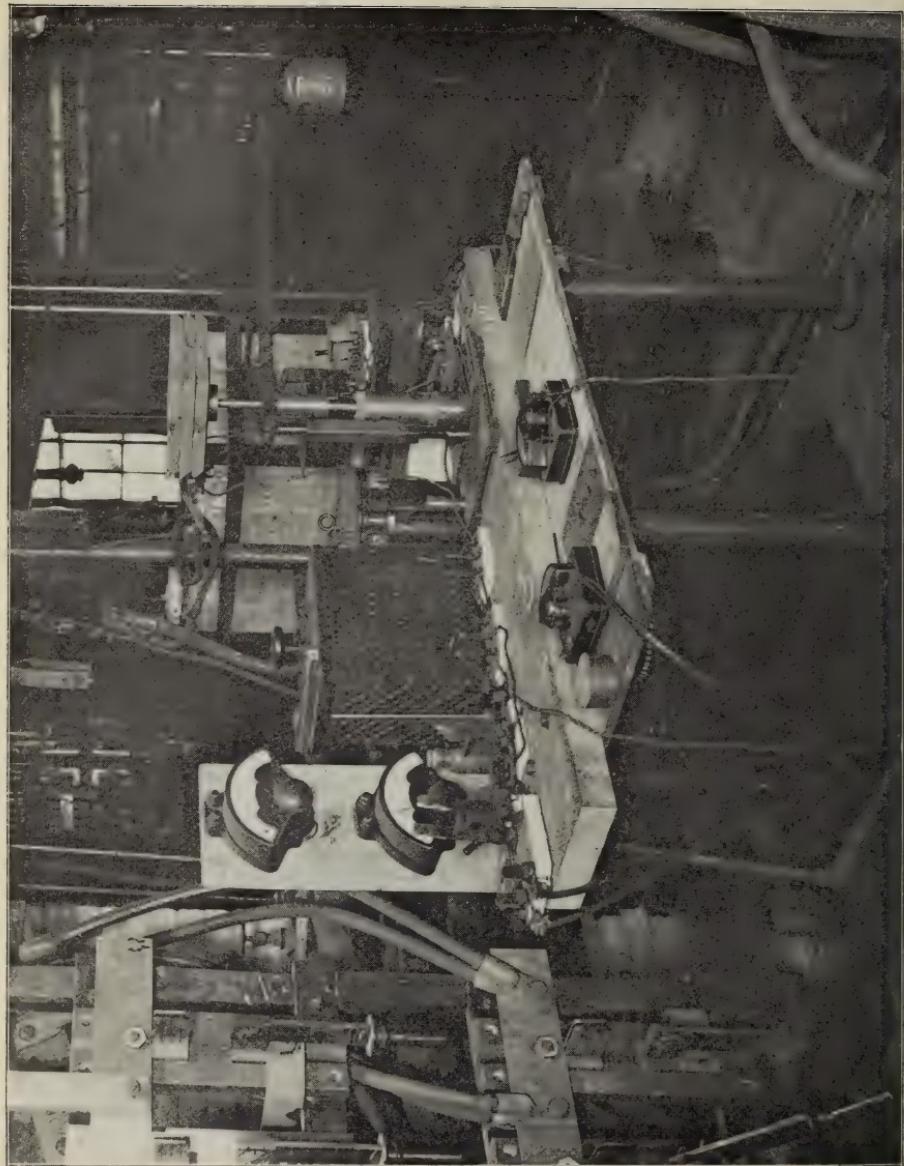


Fig. 13



METHODS OF PREPARATION OF BORON

I now come to the second part of this lecture in which I will describe briefly how we make pure fused boron, how we produce technically pure material in quantities and how we bring boron into definite shape. The methods are novel to a large extent and once developed in case of boron have shown themselves capable of important applications in other fields.

To make technically pure boron we start with the reaction which has been studied before, the reaction between boric anhydride and magnesium or alkali metals. This reaction gives different products according to the relative weights of the substances employed, the temperature and so forth. One interesting product is obtained under certain conditions which product is boron sub-oxide of the approximate formula B_6O . Under other conditions a product consisting of boron and magnesium boride is obtained. Detailed description of this reaction can be found in my article of 1909 and will not be gone into here.

This boron sub-oxide or magnesium boride compound is decomposed and the resulting boron melted in an arc. As boron sub-oxide is practically an insulator a high potential arc is used. Boron sub-oxide in a copper cup forms one electrode, the other is formed by a water-cooled copper electrode. The fusion takes place in an indifferent atmosphere, such as hydrogen. The arc is started with the two electrodes a certain distance apart by means of a high voltage, say 15,000 volts, delivering a relatively small current; when everything is heated up the voltage is changed to about 2200 volts, the current to 50 amperes. After a while it is possible to reduce the voltage to 500 volts D. C. and increase the current to the desired value; by using 200–300 amperes it is possible to melt down a few pounds of boron at once.

I will show you the small furnace which we used for some time and which is now replaced by a much bigger one. In this size of furnace only about a pound of boron can be melted in one operation.

You see (Fig. 11) the iron hood which can be moved up and down and through which hydrogen is flowing. Inside of it is a

water-cooled copper cup containing the boron sub-oxide powder. Through the top a water-cooled copper terminal passes and is insulated from the hood. A window is provided through which the operation of the furnace can be watched. The high voltage transformer is seen to the left of furnace as well as the bus bars conveying 2000 volts—50 amperes and 500–700 volts—300 amperes respectively.

In this way it was found at first impossible to make absolutely pure boron. As long as the impurities are boiling out of the boron there is no danger of contamination with the material of the upper electrode; but when the state of purity of boron is approached the danger gets considerable, and one has to stop a little short of absolute purity. With great care one can get a material containing about 99% boron. The average product will perhaps be not more than 97 to 98% boron. This product is good for some applications, but not for others.

It was necessary to develop an arc furnace in which no impurities at all would be introduced, either by chemical combination or mechanical admixture of the product of disintegration of the coöperating electrode. This has been accomplished and a furnace has been constructed in which practically any material can be melted down without introducing the slightest impurities into it. Most of the known arc furnaces use carbon electrodes or water-cooled metallic electrodes and while they are excellent for some purposes they are apt to contaminate the material to be treated. They do not give a clear heat, that is high temperature and nothing else.

The new furnace is based on the use of a mercury electrode. It is a mercury *arc* furnace in an indifferent atmosphere.

This is one way of making boron.

The other way has been developed before this one, is capable of giving absolutely pure boron but is not as well adapted for producing large quantities. This method takes for its starting point boron chloride. If boron chloride is brought together with hydrogen at a high enough temperature it is reduced to boron and hydrochloric acid. All the materials taking part in the reaction are gaseous except boron itself. As boron chloride can be made very pure and the slight impurities that may be in

it are not reduced by hydrogen, the product is chemically pure boron in the most accurate sense of the word. If boron in the form of powder or lumps is wanted the reaction is carried out in an arc discharge between copper, or better, boron terminals. For practical applications (for making regulators, cut-outs, meter jewels) where a deposit of boron is wanted the gases are passed into a vessel in which a filament or plate is brought to incandescence by current.

The simple apparatus used is shown on Figure (12). The hydrogen, freed from oxygen and dried in the usual way passes through liquid boron chloride which is kept at a definite temperature and the mixture passes then through the vessel on the left where it is caused to react by the incandescent body.

The procedure is modified in case it is desired to deposit a definite amount of boron. A vessel of definite dimensions is then filled with boron chloride and hydrogen of definite pressures.

The arc furnace delivers us irregular lumps of boron. Starting with these, how could one make a rod of boron? To cast in a mould is excluded because the melting point of boron is about 2300°C. It was found impossible to agglomerate the very hard boron by mere compression. The use of binding material would introduce impurities; but even if the material were agglomerated the subsequent sintering by current would be a difficult matter on account of the large negative temperature coefficient resistance of boron. The current has a tendency to concentrate in lines which happen to have a higher conductivity; streaks develop, causing melting through in points before the whole mass is sintered.

It was necessary to surround the boron with an envelope which would equalize the temperature, and preserve the shape. But what material is to be used for the envelope? The temperature must be high, must be around 2300°. At that temperature the material must not have an appreciable conductivity, or else it would take current itself, but above all it must not attack boron. Boron is very active at high temperatures and attacks practically everything known, all known oxides included.

The solution of the difficulty was found in the use of a boron compound—boron nitride.

If boron itself is an interesting substance, boron nitride is another. Boron nitride is described in all books of chemistry, but its physical properties have not been well known.

It is infusible. I have not succeeded in fusing boron nitride even at the temperature at which tungsten melts. More than that, boron nitride is a very poor electrical conductor at high temperature, much poorer than all other known insulators. For instance, a small disc of magnesium oxide $1/8''$ thick passed in some of my tests an appreciable current at 800°C with 110 volts applied. A disc of boron nitride of the same dimensions heated to 1200°C and put across 500 volts gave no measurable current. These two properties: infusibility and high insulating power at high temperatures, make it the ideal substance for an envelope in sintering boron.

One more thing is necessary in order to make the sintering furnace complete; it is necessary to insure good contact between the boron powder and the electrodes which conduct the current to it. This is done by applying pressure, and so a new type of furnace was developed, which we call the "boron nitride sintering furnace." With this furnace not only boron has been formed into rods but also boron carbide, tungsten, and a large number of other materials. On account of the inertness of boron nitride most any refractory material can be sintered in this furnace and it is difficult at present to oversee all the possibilities of this furnace in the direction of sintering metals or combining materials at high temperatures under high pressure.

Of course, in order to use boron nitride in this furnace we had to develop a way for making boron nitride relatively cheap and in large quantities.

A small size boron nitride furnace is shown in the figure which I now throw on the screen. (Fig. 13)

I could go on talking about boron but the lecture has gone beyond what I intended. You are all tired, or else do not want to miss the organ recital. So I thank you for your attention. (Applause.)

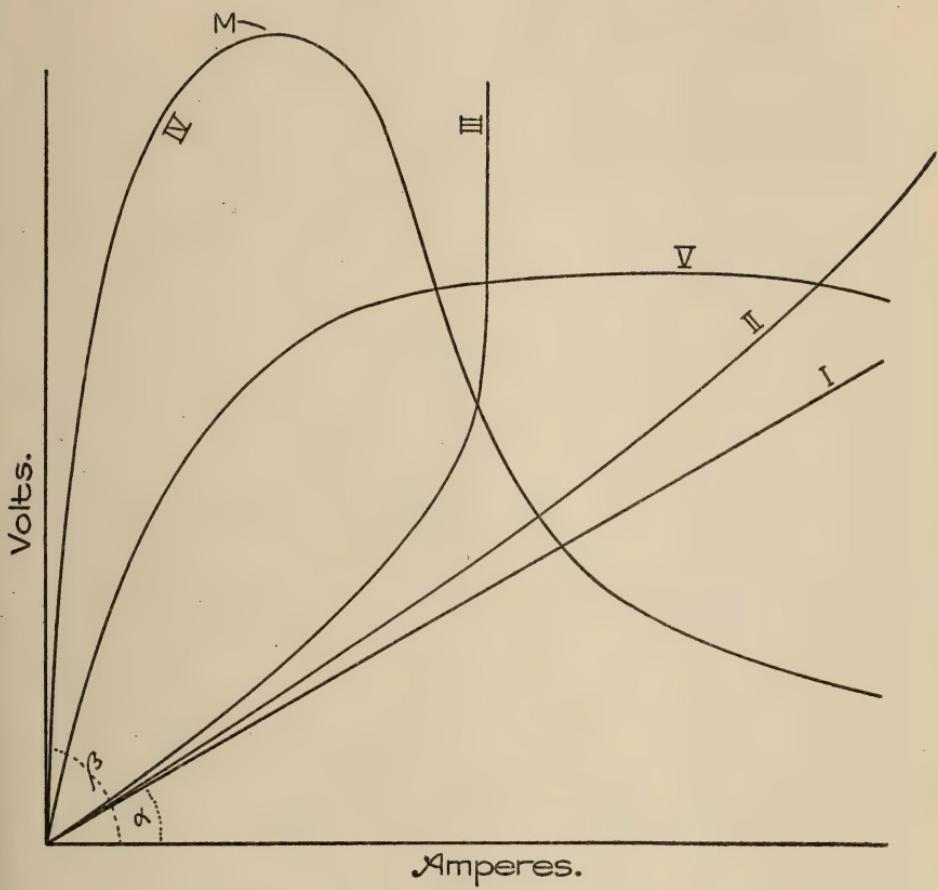


Fig. 4

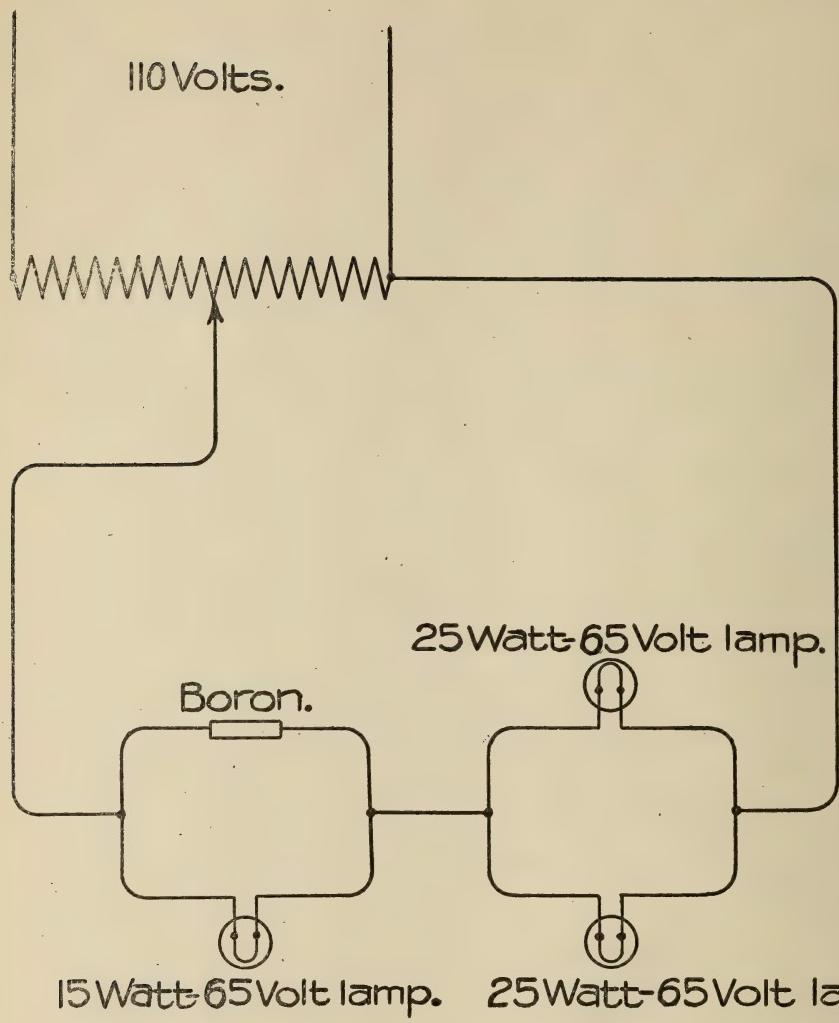


Fig. 9

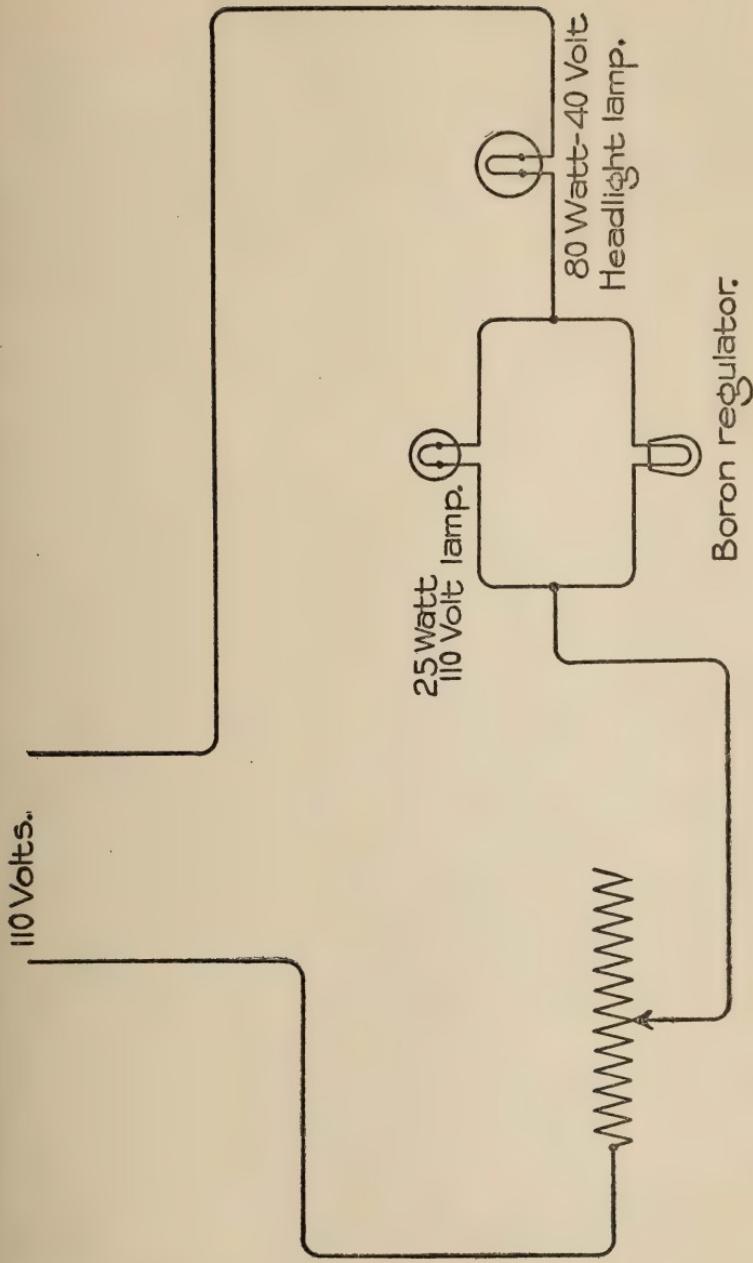


Fig. 10

(*Abstract*)

THE CONSERVATION OF THE ATMOSPHERE: THE USE AND MISUSE OF THE AIR

C. A. DAVIS

LEGAL PHASES OF RIGHTS IN AIR

J. W. THOMPSON

The air is composed of four gases, three of which only, are significant in this discussion; namely, nitrogen, oxygen, and carbon dioxide; the last is an impurity formed by the life processes of organisms, and by combustion of carbonaceous materials. Of these gases, oxygen is the only chemically active one and nitrogen a dilutent. Carbon dioxide is inert and dangerous to life only in much larger excess than exists in the air, where there are only 3 parts in 10,000 normally present.

The chief agents of exhaustion of the supply of oxygen in the air are the respiration of plants and animals, the chemical union of the gas with constituents of the earth's crust, and the combustion of fuels containing carbon. The air is rendered less pure by the development of carbon dioxide given off by combustion and organisms but a part of the gas thus formed is abstracted from the air and decomposed by green plants, the oxygen, in part, being turned back into the air.

If all of the known coal deposits of the Earth were converted into carbon dioxide, the amount would not increase the percentage to an extent to make it injurious to man.

Other impurities given off into the air as the result of the operation of chemical, manufacturing, transportation, metallurgical and technical industries, such as acid fumes, uncombined gaseous elements, soot, dust, odors and similar substances, are soon removed by rain and are only local in their effect, and,

while often very annoying to communities, do not usually affect any considerable part of the atmosphere for long.

The industry recently established for converting air nitrogen into nitrogenous compounds for use in agriculture will probably affect the air more by depriving it of oxygen than by taking from it the nitrogen used, but this use is too recent to be important as yet.

It is time that some concerted attempt was made to find out, by careful investigation, what the real status of the air resources of the Earth really are and whether for the sake of future generations more careful use be made of it in the present and near future.

LEGAL PHASES OF RIGHTS IN AIR

Every person has a right to receive and use unpolluted air as a natural right attached to all property. This right is zealously guarded by law and enforced by equity in the interest of individuals as well as the public, although slight invasions of the right do not create legal wrongs.

The law gives no remedy for mere diminution of air and recognizes no right to the flow of air.

On the highest judicial authority it is settled that a State in its sovereign capacity has an interest, independent of the titles of its citizens, in all the Earth and air within its domain, so that the air of its territory shall not be polluted on a great scale by poisonous gases by the acts of persons over whom it has no immediate control.

The law has afforded protection and given various remedies for the pollution and creation of improper conditions in the air under a great variety of subjects or heads, involving nearly every phase of industrial activity.

Much litigation has arisen from the operation of smelters and reduction works because of their generating and distributing poisonous and noxious fumes and gases. The courts have recognized the property right of unpolluted air, but have held that there can be no legal remedy for the infraction on a right unless substantial damages follow. They also recognize the rule of comparative convenience and inconvenience, with the conclusion

that in such cases injunctions cannot be decreed as an unqualified right, but should be granted or withheld according to the equities of the case; being withheld where it will necessarily operate contrary to the real justice of the case. Due consideration has been given to the comparative injury resulting from the granting or refusal of the injunction sought.

The question of the right to use the air for aerial navigation and transportation is of recent origin and has arisen in several forms, as: "Has one person the right to use or occupy for the purposes of transportation or navigation the air over the land of another?" "Does the State possess the power to regulate or prohibit navigation of the air?" Various opinions are cited laying down the limitations of the principle of superincumbent ownership of the air, and, in general, actions for trespass against aviators have been limited to an interference with the air space appurtenant to the soil.

The German Imperial Code of 1900 has the following section:

"Sec. 905. The right of the owner to a piece of land extends to the space above the surface, and to the substance of the Earth beneath the surface. The owner may not, however, forbid interference which takes place at such a height or depth that he has no interest in its prevention."

Undoubtedly, the State has the power to regulate air travel for the protection of the public, and the English Parliament passed an act for the protection of the public, during the recent Coronation ceremonies, against dangers arising from the navigation of air craft and authorizing the Secretary of State to prohibit or limit the privilege as he should prescribe by order.

Such an act assumes the power on the part of the legislative authority to license those who may sail the air; and it follows that the same authority may require licensees to give a sufficient bond to protect the public and individuals. A determination of the liability of an airship owner for injuries to the subjacent landowner would involve no new legal principles, but only the application of well established rules relating to trespass. The owner of an airship which has fallen is liable not only for the damage done by the machine but also for that caused by the curiosity seekers who may be attracted to the fallen craft.

The rights and duties of air sailors towards each other may be determined either by convention and code or by custom.

It may be confidently asserted that when air travel has passed the experimental stage and reached the fixed, though dangerous fact, the "law of the road" and the "rules of the ocean" will adjust themselves to this upper trackless element.

PATENTSCHUTZ FÜR PHARMAZEUTISCHE PRODUKTE

Bericht von Verein deutscher chemiker für den VIII. Internationalen Kongress für angewandte Chemie zu Washington und New York.

RECHTSANWALT DR. H. ISAY UND PATENTANWALT DR. J.
EPHRAIM
Berlin, Germany

Die Frage, ob und inwieweit pharmazeutische Produkte zu Patent angemeldet werden können, ist in den verschiedenen Ländern verschieden geregelt. Im allgemeinen lassen sich drei grosse Gruppen unterscheiden:

Die erste Gruppe, zu der im wesentlichen die Länder englischen Rechts gehören, enthalten überhaupt keine besonderen Bestimmungen über die Patentierung pharmazeutischer Erfindungen.

Die zweite und Hauptgruppe bilden diejenigen Länder, welche den Stoffschutz für pharmazeutische Produkte ausschliessen, dagegen das Herstel Lungsverfahren für patentfähig erklären.

Eine dritte Stellung nimmt Russland ein, welches pharmazeutische Erfindungen schlechthin vom Patentschutz ausnimmt, sowohl was den Stoff, wie was das Herstellungsverfahren und die Apparate hierzu angeht.

Innerhalb der zweiten Gruppe nimmt die Schweiz noch eine Sonderstellung ein, insofern, als sie die Herstellung von Arzneimitteln nur soweit für patentfähig erklärt, als diese auf chemischem Wege erfolgt, und ferner insofern sie den Patentschutz auf eine kürzere Zeit als bei anderen Patenten, nämlich auf 10 Jahre beschränkt. Ebenfalls eine Sonderstellung hat Frankreich, welches bezüglich Geheimmitteln auf ein altes Dekret vom 18. August 1810 verweist, wonach die Ankündigung und der Verkauf von Geheimmitteln verboten sind.

Die übergrosse Mehrzahl aller Patentländer steht auf dem

gleichen Standpunkt wie das deutsche Recht, wonach das Herstellungsverfahren, nicht aber das Produkt pharmazeutischer Erfindungen patentfähig ist.

Das deutsche Gesetz knüpft die Patentfähigkeit des Herstellungsverfahrens an das Erfordernis, dass ein "bestimmtes Verfahren" vorliegen muss, ein Erfordernis, das im übrigen ja auch für die chemischen Erfindungen gilt.

Es fragt sich, was damit gesagt werden soll. In dieser Hinsicht bestehen verschiedene Ansichten, die kürzlich noch von Schanze in Januarheft der Zeitschrift "Gewerblicher Rechtschutz" Seite 35 ff. zusammengestellt sind.

Speziell für pharmazeutische Erfindungen sind nun mehrere Entscheidungen des Patentamts ergangen, welche einer kurzen Erörterung zu unterziehen sind:

In einem Falle handelt es sich darum, ein in der Natur vorkommendes Produkt zu einem Arzneimittel zu verarbeiten. Das Naturprodukt war ein Gemisch verschiedener Körper, und es ergab sich bei seiner Untersuchung, dass nur eines oder mehrere dieser Bestandteile wirksam war, während die anderen entweder überhaupt keine Wirkung hatten oder unerwünschte Erscheinungen hervorriefen. Ein Verfahren aus diesem bekannten Naturprodukt durch eine Reinigung das besonders wirksame Element auszuscheiden, um dadurch eine erhöhte therapeutische Wirkung hervorzurufen, wurde vom Patentamt für nicht patentfähig erklärt, da es nicht ein im Sinne des § 1 Ziffer 2 des Patentgesetzes neues und bestimmtes Verfahren sei (E. 15919 IV/30 vom 11. Februar 1911). In einem anderen Falle handelte es sich darum, dass ein neuer Stoff mit einem Oel gemischt wurde, um ein bisher unbekanntes Arzneimittel zu erhalten. Die Anmedeabteilung versagte das Patent mit folgender Begründung: (W. 27962 IV/30 h).

"Mit Recht ist im Vorbescheid die Patentfähigkeit des Anmeldungsgegenstandes mit dem Hinweis darauf bestritten worden, dass ein bestimmtes Verfahren zur Herstellung eines Arzneimittels nicht vorliege, denn wenn auch die Behauptung des Patentsuchers glaubhaft ist, dass nach der Anmeldung ein von den Ausgangsmaterialien verschiedenes Produkt, nämlich eine Lösung von X in Oel vorliegt, so beruht doch, wie der Anmelder selbst angibt,

die Erzeugung des X Oels auf der bekannten 'Einwirkung von X auf Oel.'

In den hier fraglichen Fällen ist allerdings in den Bescheiden des Patentamts der Gesichtspunkt, dass kein bestimmtes Verfahren vorliege, mit dem Gesichtspunkt, dass das Verfahren der Neuheit und Eigenart entbehre, verquickt worden, während selbstverständlich beide Gesichtspunkte scharf auseinander zu halten sind. Es kann ein bestimmtes Verfahren bekannt und es kann ein allgemeineres Verfahren neu sein.

Dass in den hier vorgetragenen Fällen das Verfahren ein bestimmtes ist, kann aber nicht wohl bestritten werden. Damit ein Verfahren als bestimmt angesprochen werde, ist nichts weiter erforderlich, als dass die verwendeten Stoffe und die Art und Weise ihrer Behandlung derartig gekennzeichnet ist, dass ein Fachmann ohne irgend welche eigene erfinderische Tätigkeit nach der gegebenen Kennzeichnung in der Lage ist, das Verfahren anzuwenden.

In diesem Sinne ist im übrigen auch kürzlich erst eine Entscheidung des Reichsgerichts ergangen. Es handelte sich dort um die Frage, ob, wenn der Patentschutz sich nur auf ein bestimmtes Verfahren erstreckt, schon dann das Patent verletzt werde, wenn nur die gleichen Ausgangsstoffe benutzt werden, während die Art ihrer Verbindung abweichend von der im Patent genannten erfolgt. Das Reichsgericht hat in der Entscheidung vom 13. Dezember 1911 (Das Recht 1912 No. 505) angenommen, dass für ein bestimmtes Verfahren im Sinne des §1 die Art der Verbindung der Ausgangsstoffe dann nicht als wesentliches Merkmal anzusehen sei, wenn "sich dieser Weg ohne schöpferische Geistesstätigkeit ohne weiteres aus naheliegenden Massnahmen der gewöhnlichen chemischen Konstruktion ergebe."

In dieser Hinsicht sind also für pharmazeutische Erfindungen keine anderen Bedingungen als wie für chemische Erfindungen einzusehen, und wenn man auch im einzelnen zweifelhaft sein kann, so sind doch im grossen ganzen für die Frage, ob ein bestimmtes Verfahren im Sinne des §1 des Patentgesetzes vorliegt, die vom Reichsgericht aufgestellten Gesichtspunkte als zutreffend anzuerkennen.

Eine weitere Frage ist die, ob die therapeutischen Wirkungen

eines Heilmittels als patentbegründend für das Herstellungsverfahren angesehen werden können.

Das Patentamt hat lange Zeit auf dem Standpunkt gestanden, dass bei pharmazeutischen Erfindungen gerade die therapeutischen Wirkungen als patentbegründend anzusehen seien. Es ist aber zweifelhaft, ob dieser Standpunkt heute noch voll aufrecht erhalten wird. In einer Entscheidung vom 22. Mai 1911 betreffend die Herstellung eines Arzneimittels, welches Eisen, Chinasäure und Albumin enthält, hat das Reichsgericht folgendes erklärt:

“Die angeblich günstigen therapeutischen Wirkungen der Chinasäure können für die Aufrechterhaltung des Patentes nicht verwertet werden, denn es handelt sich hierbei um Wirkungen der Chinasäure als Arzneimittel. Arzneimittel können aber nach §1 Ziffer 2 des Patentgesetzes nicht Gegenstand eines Patentes sein. In dem Verfahren *zur Herstellung* des Eisenpräparates aber kommen die therapeutischen Wirkungen nicht zur Geltung.” (Blatt für Patentwesen 1911 Seite 42.)

Dieser Auffassung muss aber auf das bestimmteste widersprochen werden. Für die Frage, ob die therapeutische Wirkung, d. h. die Brauchbarkeit, patentbegründend sein kann, ist es ganz unerheblich, in welcher Weise der Gegenstand der Erfindung formuliert worden ist. Für diese Frage kommt die Erfindung als Ganzes in Betracht, und die Erfindung als Ganzes besteht immer in der Erreichung eines technischen Effekts zur Befriedigung eines bestimmten Bedürfnisses. Die Patentfähigkeit braucht nun durchaus nicht immer in der Art und Weise zu liegen, wie der technische Effekt erzielt wird, sie kann auch in der Befriedigung des bestimmten Bedürfnisses, in der Brauchbarkeit liegen (vgl. Isay II. Aufl. Anmerkung 27 zu §1). Dies ist auch vom Reichsgericht wiederholt anerkannt worden. Wenn daher durch ein Verfahren, welches an sich weder neu noch erfinderisch ist, ein Stoff hergestellt wird, der besondere therapeutische Wirkungen hat, so ist die Herstellung dieses Stoffes als patentfähig in Anspruch zu nehmen.

Auch in dieser Hinsicht kann daher den pharmazeutischen Erfindungen irgend eine Sonderstellung nicht eingeräumt werden.

DER AKZESSORISCHE CHARAKTER DES MARKENSCHUTZES

Bericht vom Verein deutscher Chemiker für den VIII. Internationalen Kongress für angewandte Chemie zu Washington und New York

PROFESSOR DR. JUR. ET PHIL. E. KLOEPPEL
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Das erste deutsche Markenschutzgesetz vom 30. November 1874 vertrat inbezug auf den Schutz der Ausländermarke konsequent die Theorie des individualrechtlichen Charakters der Marke; demgemäß enthielt der § 20 dieses Gesetzes folgende Bestimmungen:

“2. Mit der Anmeldung ist der Nachweis zu verbinden, dass in dem fremden Staate die Voraussetzungen erfüllt sind, unter welche der Anmeldende dort einen Schutz für das Zeichen beanspruchen kann;

3. Die Anmeldung begründet ein Recht auf ein Zeichen nur insofern und auf so lange, als in dem fremden Staate der Anmeldende in der Benutzung des Zeichens geschützt ist.”

Auf Grund dieser Bestimmungen hat auch die damalige Rechtsprechung diesen Grundsatz ganz scharf durchgeführt.¹ Eine wesentliche Abschwächung dieses Prinzips brachte dann das neue deutsche Warenzeichengesetz vom 12. Mai 1894, das in seinem § 23 Abs. 3 folgendes bestimmt:

“Wer ein ausländisches Warenzeichen zur Anmeldung bringt; hat damit den Nachweis zu verbinden, dass er in dem Staate, in welchem seine Niederlassung sich befindet, für dieses Zeichen den Markenschutz nachgesucht und erhalten hat. Die Eintragung ist, soweit nicht Staatsverträge ein Anderes bestimmen, nur dann zulässig, wenn das Zeichen den Anforderungen, dieses Gesetzes entspricht.”

¹vergl. Osterrieth, Gewerblicher Rechtsschutz und Urheberrecht 1903 S. 67.

Danach ist die Existenz des Auslandsschutzes nur noch für die *Eintragung* des Zeichens massgebend, für den Fortbestand desselben dagegen ohne Bedeutung, indem ein einmal eingetragenes Zeichen eines Ausländer aus dem Grunde, weil der Schutz im Auslande erloschen ist, später in Deutschland nicht mehr gelöscht werden kann.¹

Damit ist ferner aber auch, wie *Osterrieth* in seinem vor Kurzem erschienenen Bericht über die Washingtoner diplomatische Konferenz vom Summer 1911² zutreffend hervorhebt, der Grundsatz des akzessorischen Charakters gegenüber allen denjenigen Ländern mit reinem Anmeldeverfahren, wo also die Eintragung ohne jede sachliche Prüfung erfolgt, materiell aufgehoben.

Wir befinden uns also in Bezug auf die Behandlung der Ausländermarke in einem Zustand der Halbheit und es wird auch in den beteiligten Kreisen heute allgemein der Wunsch vertreten, den Grundsatz des akzessorischen Charakters des Markenschutzes zum mindesten innerhalb des Geltungsbereichs der Pariser Konvention zu beseitigen.³

Ueber die Frage nun, inwieweit die Pariser Konvention für ihren Geltungsbereich den fraglichen Grundsatz beseitigt hat, bestehen bisher zwei Auffassungen. Nach der einen, die wir kurz als die französische bezeichnen können, wird der Pariser Konvention jede Wirkung in dieser Beziehung abgesprochen, nach der anderen, die insbesondere *Osterrieth* in seinem oben zitierten Aufsatz von 1903 sehr eingehend begründet hat, wird angenommen, dass durch das in Art. 2 der Pariser Konvention festgelegte Grundprinzip der Gleichstellung des Ausländers mit dem Inländer die gegenstehenden Bestimmungen der einzelnen Warenzeichengesetze, insbesondere des § 23 des deutschen Gesetzes, beseitigt seien.

Sehr mit Recht hat zur Beseitigung dieser Unklarheit die deutsche Regierung auf der Washingtoner Konferenz (vergl. den schon zitierten *Osterrieth*' schen Bericht S. 46 ff.) einen Antrag gestellt, durch Einfügung einer ausdrücklichen Bestimmung in

¹vergl. z. B. *Seligsohn*, Kommentar zum Warenzeichengesetz, II. Aufl. S. 268.

²Berlin, Carl Heymanns Verlag 1912 S. 50151.

³vergl. *Kloepfel*, die Grundlagen des Markenschutzes, Berlin 1911 S. 44.

die Pariser Konvention den Grundsatz das akzessorischen Charakters für das Gebiet dieses Staatsvertrages vollständig zu beseitigen. Die Berechtigung dieses Bestrebens der deutschen Regierung bedarf heute kaum noch einer näheren Begründung. Die Verhältnisse auf dem Gebiet des internationalen Rechtsschutzes haben sich, insbesondere auch für Deutschland, durch die Entwicklung seines Exporthandels im Laufe der Jahre soweit geändert, dass die Marke ihren individualrechtlichen Charakter, also die Funktion, in erster Linie auf die Person ihres Urhebers hinzuweisen, weitgehend verloren hat.

Schon in seinem erwähnten Aufsatz von 1903 führte *Osterrieth* in dieser Beziehung sehr zutreffend aus: "Unsere grossen Exportfirmen haben hunderte von Marken, die allein für den ostasiatischen, den chinesischen oder japanischen Markt bestimmt sind, die für Deutschland aber gar keine Bedeutung haben. Gerade für diesen ostasiatischen Markt werden als Marken häufig Devisen gewählt, denen der europäische Konsument kein Verständnis entgegenbringt, und in denen er keine Unterscheidungskraft finden würde. Bei der Kundschaft im fernen Asien dagegen verkörpert sich in diesen Marken der Ruf der Firma, ja sogar die Firma selbst, ohne dass die Kunden wissen oder zu wissen brauchen, wo die Firma ihre Niederlassung hat. . . . Es ist in der Tat nicht abzusehen, warum ein Geschäftsmann, der ein Zeichen nur in einem ganz bestimmten Lande, z. B. in Japan, gebrauchen will, gezwungen sein soll, die Marke so auszuwählen, als wenn er sie in seinem Heimatlande, d. h. am Sitze der Niederlassung und nur von da aus in allen anderen Ländern gebrauchen wollte."

Bei den Beratungen auf den Kongressen der Internationalen Vereinigung für gewerblichen Rechtsschutz über die Frage hat, wie auf dem Kongress zu Brüssel 1910¹ der Generalberichterstatter *Georges Maillard* zusammenfassend dargelegt hat, die Vereinigung wiederholt den Grundsatz der Unabhängigkeit der Marke ausgesprochen. *Maillard* hat in seinem erwähnten Bericht die Notwendigkeit der Beseitigung des akzessorischen Charakters noch einmal eingehend begründet. Der Brüsseler

¹Annuaire de l'Association internationale pour la protection de la propriété industrielle 1910 S. 133 ff.

Kongress hat dann einstimmig einen Beschluss gefasst, der genau dem Antrag entspricht, den die deutsche Regierung in Washington gestellt hat.

Nachdem auf den Kongressen der Internationalen Vereinigung die französischen Mitglieder regelmässig zahlreich vertreten waren, hätte man im Hinblick auf die Einstimmigkeit der Beschlüsse erwarten können, dass der Antrag der deutschen Regierung auch auf der Washingtoner Konferenz ohne weiteres angenommen würde. Ueerraschenderweise kam dieser Antrag in Washington aber doch zu Fall, und zwar in erster Linie, weil er von den *französischen* Vertretern auf das Entschiedenste bekämpft wurde. Es wurde von der französischen Vertretung besonders darauf hingewiesen, dass dieser Antrag das Grundprinzip der Pariser Konvention, das auf der Theorie des "Personalstatuts der Marke" (also auf dem Grundsatz des "individualrechtlichen Charakters" derselben) aufgebaut sei, erschüttere (*Osterrieth* 1. c. S. 49). Aus diesem Grundsatz ergebe sich, dass man eine Marke nicht schützen könne, die nicht vorschriftsmässig im Ursprungslande eingetragen sei; auch dürfe grundsätzlich niemand im Auslande weitergehende Rechte beanspruchen, als er sie im Heimatlande besitze. Trotzdem die deutsche Auffassung von den Vertretern Englands, Italiens, Österreichs und der Vereinigten Staaten unterstützt wurde, kam der deutsche Antrag bei der Abstimmung zu Fall. Damit ist zweifellos eine ganz neue Lage auf dem Gebiet des internationalen Markenrechts geschaffen. Statt dass der akzessorische Charakter aufgegeben oder gemildert worden wäre, ist gerade durch Ablehnung des deutschen Antrags dieser Grundsatz indirekt als heute für die Pariser Konvention absolut massgebend hingestellt worden.

Umso energischer müssen also die Gegner des akzessorischen Charakters heute den Wunsch betonen, dass dieser Grundsatz sobald als möglich beseitigt werden muss. Die blosse theoretische Verfechtung dieses Wunsches dürfte aber gerade im Hinblick auf die Ergebnisse der Washingtoner Konferenz heute einen recht platonischen Charakter haben. Sehr mit Recht hat daher die Kommission für internationalen Rechtsschutz des Deutschen Vereins für den Schutz des gewerblichen Eigentums in ihren vor

Kurzem abgehaltenen Beratungen über diese Frage sich auf den Standpunkt gestellt, dass dem Deutschen Reich und ebenso allen anderen Staaten, die den Wunsch hegen, zu einer *internationalen* Beseitigung des akzessorischen Charakters zu gelangen, nichts anderes übrig bleibe, als nunmehr einerseits in ihren *nationalen* Gesetzgebungen diesen Grundsatz umso *schärfer* zum Ausdruck zu bringen, andererseits aber gleichzeitig mit dieser Verschärfung ihre Bereitwilligkeit zur Beseitigung dieser verschärften Bestimmung im Vertragswege zu erkennen zu geben. Die genannte Kommission hat daher vor Kurzem einstimmig den Beschluss gefasst, dass dem Abs. 3 des § 23 des deutschen Gesetzes bei der bevorstehenden Revision folgende Fassung gegeben werden möge:

“Die Eintragung und der Schutz eines ausländischen Zeichens sind davon abhängig, dass das Zeichen in dem Staate, in welchem die Niederlassung des Anmelders sich befindet, vorschriftsmässig *eingetragen ist* und gemäss der Gesetzgebung dieses Landes *auch tatsächlichen Schutz geniesst.*”

Diese Bestimmung verfolgt also den Zweck, die heute, wie schon oben erwähnt, gegenüber den Ländern mit reinem Anmeldesystem nur noch formell bestehende Reciprozität auch materiell durchzuführen. Man ging bei dem fraglichen Beschluss sehr mit Recht von dem Gedanken aus, dass eine schärfere Handhabung des akzessorischen Charakters gegenüber denjenigen Staaten, die den deutschen Antrag zu Fall gebracht haben, jedenfalls dahin führen werde, dass die Interessenten der betreffenden Länder sich besinnen und bald selbst darauf dringen würden, dass ihre Regierungen ihren sachlich unbegründeten Widerstand gegen den erwähnten deutschen Vorschlag aufgeben. Um mit denjenigem Staaten, die heute bereits auf dem deutschen Standpunkt stehen, schon bald zu einer Verständigung kommen zu können, hat die Kommission sich weiter dahin ausgesprochen, dass (entsprechend der Novelle zum deutschen Patentgesetz von 1911) in dem neuen Warenzeichengesetz bestimmt werden solle, dass von dem Erfordernis der Eintragung und des Schutzes im Ursprungslande abgesehen werden könne gegenüber solchen Ländern, die den deutschen Markeninteressenten Reciprozität gewähren. Damit wäre dann im Gesetz eine Basis geschaffen, auf Grund deren im Wege von Staatsverträgen (eventuell auch

durch Abschluss einer engeren Konvention innerhalb des Rahmens der grossen Pariser Konvention) der Grundsatz der Unabhängigkeit des Markenschutzes die erwünschte Anerkennung erhalten würde.

Diese Vorschläge des Deutschen Vereins sind für die nationale Behandlung der Frage sehr beachtenswert.

Bei der internationalen Behandlung empfiehlt es sich, solange eine Abhilfe für die ganze Konvention nicht zu erzielen ist, wenigstens schon durch Gegenseitigkeitsverträge zwischen den einzelnen Konventionsstaaten eine Abhilfe zu schaffen. Dieses Bestreben würde durch eine entsprechende Beschlussfassung unseres Internationalen Kongresses eine wesentliche Förderung erhalten.

AUSÜBUNGS-UND LIZENZZWANG

*Bericht vom Verein deutscher Chemiker für den VIII.
Internationalen Kongress für angewandte Chemie
zu Washington und New York*

RECHTSANWALT W. MEINHARDT I
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Zum Wesen des Patentschutzes gehört das ausschliessliche Recht der Ausnutzung der patentierten Erfindung. Jede Monopolstellung aber beeinträchtigt das Recht der Allgemeinheit; diese zu schützen, ist Aufgabe jedes Staates. Als einen solchen Schutz haben nun die meisten Staaten den Ausübungszwang und den Lizenzzwang angesehen.

Unter ersterem verstehen wir die Verpflichtung des Patentinhabers, den Gegenstand der Erfindung in demjenigen Lande herzzutellen, das ihm den Patentschutz verliehen hat; unter "Lizenzzwang" die Verpflichtung, Dritten die Ausnutzung der Erfindung im Inlande gegen Zahlung einer angemessenen Vergütung zu gestatten.

Eine vergleichende Zusammenstellung der auf dem Gebiete des Ausübungs- und des Lizenzzwanges zum Schutze der Allgemeinheit getroffenen Bestimmungen—die sich in dem knapp gespannten Rahmen des vorliegenden Berichts umso mehr erübrigt, als sie sich in den meisten Lehrbüchern des Patentrechts findet, also jedem Interessenten ohne Schwierigkeiten zugänglich ist—, zeigt nicht nur, dass die einzelnen Staaten hinsichtlich der Durchführung der gedachten Schutzmassregeln von einander erheblich abgewichen sind, sondern auch, dass über die Wirksamkeit dieser Schutzmassregeln die Ansichten schon vor Jahren sehr geteilt gewesen sind.

Wir finden somit Länder, welche den Ausübungszwang vollständig verwerfen (Amerika) und solche, welche in der möglichst straffen Durchführung derselben ihre protektionistischen

Wünsche zu verwirklichen glaubten (Belgien, Frankreich). In Frankreich hat bereits die Einführung auch nur eines im Auslande hergestellten Patentobjektes durch den Patentinhaber den Verfall des Patentes zur Folge.

Zwischen diesen Extremen finden wir Schutzbestimmungen, welche lediglich darauf abzielen, die Monopolstellung durch Lizenzzwang zu Gunsten der heimischen Industrie zu mildern (so England und Oesterreich vor ihrer Patentnovelle) und schliesslich solche, welche zwar den Ausführungzwang als solchen verwerfen, an die ausschliessliche oder hauptsächliche Ausführung im Auslande aber den Rechtsnachteil der Zurücknahme des Patentes knüpfen (Deutschland und England in ihren Novellen zum Patentgesetz).

Bei der Buntscheckigkeit der Bestimmungen einerseits und bei dem von allen Kulturstaaten stets als notwendig und berechtigt erkannten Streben nach internationalen Regeln auf dem Gebiet des Patentwesens andererseits setzten die Bemühungen, auch auf dem Gebiet des Ausführungs- und Lizenzzwanges internationale Vereinbarungen zu treffen, bereits früh ein, sie haben aber be-dauerlicherweise bis heute einen nennenswerten Erfolg nicht erzielt.

Bereits die Pariser Konvention vom 20. März 1883 befasst sich mit dem Ausführungzwang, sie beseitigte jedoch zunächst nur die sogenannte Einfuhrklausel und bestimmt in Art. 5 Abs. 1:

“Die durch den Patentinhaber bewirkte Einfuhr von Gegenständen, welche in einem oder dem anderen Verbandsstaate hergestellt sind, in das Land, in welchem das Patent erteilt worden ist, soll den Verfall des letzteren nicht zur Folge haben.”

Die Regelung des Ausführungzwanges als solchen licht sie dagegen ab indem sie im Absatz 2 des Artikels 5 fortfährt:

“Gleichwohl soll der Patentinhaber verpflichtet bleiben, sein Patent nach Massgabe der Gesetze des Landes, in welches er die patentierten Gegenstände einführt, auszuüben.”

Erst 17 Jahre später, in den Brüsseler Zusatzakte vom 14. Dezember 1900 gelang es, insofern eine mildere Auffassung zur Geltung zu bringen, als nunmehr dem Schlussprotokoll folgende unter 3^b hinzugefügt wird:

“Der Verfall eines Patentes wegen Nichtausübung soll in jedem

Lande nicht vor Ablauf von drei Jahren seit der Hinterlegung des Gesuches in dem Lande, um das es sich handelt, und nur dann ausgesprochen werden können, wenn der Patentinhaber rechtfertigende Gründe für seine Untätigkeit nicht dartut."

Hiernach sind also der Gesetzgebung der einzelnen Vertragsstaaten lediglich zwei Grenzen gezogen: Die Rücknahme des Patents wegen Nichtausübung darf nicht vor Ablauf von drei Jahren seit der Patentanmeldung erfolgen; dies bedeutet nicht eine etwa eine Befreiung vom Lizenzzwang während der drei Jahre, die Bestimmung bezweckt lediglich, die Gesetzgebung der einzelnen Vertragsstaaten zu verhindern, die Folgen der Nichtausübung schon vor Ablauf einer angemessenen Respektsfrist auszusprechen. Ferner soll die Nichtausübung dann ohne Einfluss auf den Bestand des Patentes sein, wenn der Patentinhaber Gründe dartut, welche seine Untätigkeit zu rechtfertigen geeignet sind.

Als solche Gründe sind in der Rechtsprechung der Verbandsstaaten angesehen worden: Unmöglichkeit der Beschaffung von Rohstoffen, Arbeitsmitteln, Arbeitskräften, Ünvollkommenheit der Erfindung, Fehler inländischen Bedarfs, Ueberholung der Erfindung durch eine bessere und dergl.

Abgesehen von den vorerwähnten Einschränkungen sind aber auch die Verbandsstaaten in der Gestaltung ihrer inneren Gesetzgebung auf dem hier erörterten Gebiet vollständig frei und sie haben auch in der Folgezeit hiervon, meines Erachtens nicht immer zum Vorteil des Ganzen, ausgiebigen Gebrauch gemacht. Denn während wir auf der einen Seite in der weiteren Entwicklung der Frage nunmehr das Streben erkennen können, auf dem einmal betretenen Wege weiter zu arbeiten und eine internationale Ausgestaltung des Ausführungs- und Lizenzzwanges herbeizuführen, sehen wir auf der anderen Seite, wie in einigen Ländern das protektionistische Bestreben immer mehr die Oberhand gewinnt und zur Verschärfung der Ausführungswangsbestimmungen im Wege der Sondergesetzgebung führt.

An der Spitze der Vorkämpfer, nicht nur für eine einheitliche, sondern auch für eine möglichst freie Ausgestaltung des Ausführungszwanges steht die "Internationale Vereinigung für den gewerblichen Rechtsschutz." Die Anregung ging im Jahre 1896 vom Deutschen Verein für den Schutz des gewerb-

lichen Eigentums aus, dessen langjähriger Führer Julius von Schütz durch seinen Vortrag:

“Inwieweit wirkt der Ausführungszwang für Erfindungen fördernd oder hemmend auf die Industrie eines Landes?” für weite Kreise den Nachweis gebracht hatte, dass die protektionistischen Bestrebungen einiger Staaten nur scheinbar die Industrie ihres Heimatlandes durch den Ausführungszwang schützten und dass das amerikanische Prinzip der vollständigen Freiheit hinsichtlich der Ausübung das einzig Richtige sei.

Seit dieser Zeit gehört die Frage zum eisernen Bestand der Kongresse der Internationalen Vereinigung für gewerblichen Rechtsschutz. Auf all diesen Kongressen wurde mit grossen Mehrheiten der Ausführungszwang im internationalen Verkehr als schädlich und unnötig bezeichnet.

Die Kongresse stellten sich durchweg auf den Standpunkt, dass der Ausführungszwang vollständig aufzuheben sei; fand sich hierfür auf den Kongressen in Wien und London (1898 und 1899) bereits eine erhebliche Mehrheit, so ist es charakteristisch, dass gerade der Pariser Kongress vom Jahre 1900, der also im Lande des starren Ausführungszwanges tagte und der infolgedessen viele berufene Vertreter der französischen Interessentenkreise zu seinen Mitgliedern zählte, *einstimmig* sich für die Abschaffung des Ausführungszwanges aussprach.

Wenn die genannte Vereinigung, deren Beruf zur Vertretung aller interessierter Industrien auf dem Gebiete des gewerblichen Rechtsschutzes von ernster Seite bisher niemals angezweifelt worden ist, in der Folgezeit ihren Standpunkt insofern geändert hat, als sie nicht mehr die Aufhebung schlechthin, sondern nur die Beseitigung der Zurücknahme infolge Nichtausführung fordert, so ist hierfür nicht eine Änderung in den Anschauungen, sondern lediglich der Gesichtspunkt massgebend gewesen, eine Formel zu finden, welche eine Zustimmung auch der heftigsten Widersacher erhoffen lässt.

Diese Hoffnungen sind nun allerdings bisher in empfindlicher Weise getäuscht worden.

Zwar ist Deutschland fortgefahren, auf dem bereits durch die Abkommen mit der Schweiz und Italien vom Jahre 1892 betretenen Wege die Frage des Ausführungszwanges durch

Staatsverträge mit Einzelstaaten im Sinne der Bestrebungen der Internationalen Vereinigung zu lösen, das Deutsche Reich hat auch neuerdings sein Patentgesetz geändert, indem es, abgesehen von dem Falle, dass die Erfindung ausschliesslich oder hauptsächlich ausserhalb seiner Grenzen ausgeführt wird, die Wirkung der Zurücknahme wegen Nichtausübung beseitigt, andere Staaten haben dagegen die Bestimmungen hinsichtlich des Ausführungszwanges verstärkt, so Oesterreich und Schweden. England, das eine Zwangslizenz nur in der allermildesten Form, den Ausübungszwang selbst aber nicht kannte, hat durch Gesetz vom 28. August 1907 diesen insofern eingeführt, als es in Uebereinstimmung der dem englischen Gesetz entnommenen Neuerung Deutschlands die Zurücknahme des Patents als zulässig bezeichnete, wenn der patentierte Artikel oder das patentierte Verfahren ausschliesslich oder in der Hauptsache im Auslande hergestellt bzw. ausgeführt ist.

Dieses Verhalten einer Grossmacht, die bisher viele Jahre hindurch auf dem denkbar freiesten Standpunkt gestanden hatte ist naturgemäss geeignet, die Bestrebungen auf Abschaffung bezw. internationale Regelung des Ausübungszwanges auf unabsehbare Zeit zu vereiteln.

Als Folge dieses ist es daher wohl auch in erster Linie mit anzusehen, dass die Bestrebungen Deutschlands und Amerikas hinsichtlich der Milderung des Ausführungszwanges auf der vorjährigen Washingtoner Konferenz zur Revision der Pariser Uebereinkunft für gewerblichen Rechtsschutz auf den lebhaftesten Widerspruch stiessen.

Die—Gründe, welche sowohl die französische als auch die grossbritannische Regierung zur Rechtfertigung ihres Widerspruchs anführt-das Nähere vergl. bei Osterrieth: Die Washingtoner Konferenz, Berlin, Carl Heymanns Verlag 1912—vermögen jedoch nicht zu überzeugen.

Es ist unrichtig, dass—wie der französische Vertreter erklärt—der Ausübungszwang eine Wohltat, eine Quelle der Kraft und des Wohlstandes für ein Land sei. Bereits früher ist wiederholt und ohne ernsthaften Widerspruch gerade auch in Frankreich, wie das oben mitgeteilte Ergebnis des Pariser Kongresses vom Jahre 1900 beweist, festgestellt worden, dass der Ausführungs-

zwang lediglich gerechtfertigt erscheinen könnte unter dem Gesichtspunkt der Vermehrung von Arbeitsgelegenheit, dass aber auch dieser Grund vielfach nur ein scheinbarer ist, weil die Einführung von Erfindungen in die Industrie zunächst grosse Opfer erfordert, die niemand aufwendet, der nicht durch eine Monopolstellung für den Fall der Bewährung der Erfindung entschädigt wird. Wer keinen Schutz auf die Neuerung hat, denkt gar nicht daran, das Risiko für die Ausprobierung und Einführung der Neuerung zu übernehmen, um dann zu erfahren, dass sich die Konkurrenz mühelos und kostenlos die Früchte seiner Arbeit zu eigen macht.

Die Gesichtspunkte wirtschaftlich-politischer Natur, die der Vertreter Grossbritanniens geltend gemacht hat, und die selbstverständlich das Verhalten als solches zu rechtfertigen geeignet sind, können naturgemäß für die Frage der Zweckmässigkeit an sich nicht in Betracht kommen.

Der Umstand, das starke Strömungen der öffentlichen Meinung die englische Regierung zu ihrem Standpunkt veranlasst haben, beweist noch nicht, dass dieser Standpunkt materiell gerechtfertigt ist.

Es ist allgemein bekannt, wie diese starken Ströme sich entwickelt haben. Es wurde von interessierter Seite mobil gemacht gegen die starke Einfuhr der deutschen chemischen Grossindustrie, die infolge ihrer Patente die Fabrikation in England zur Deckung des englischen Bedarfs allerdings in mancher Beziehung verhinderte. Die weitere Entwicklung hat aber gezeigt, dass durch die Aenderung der Gesetzgebung der Allgemeinheit im Sinne der oben erwähnten Strömungen doch nicht gedient worden ist, sondern dass die angeblichen Wohltaten des Ausübungzwanges nur einem ganz beschränktem Kreise zu gute kommen, Wohltaten, die die Nackenschläge, welche englische Erfinder naturgemäß im Auslande erhielten, nicht aufzuwiegen in der Lage sind.

Berücksichtigt man noch, dass auf der Washingtoner Konferenz der Vertreter Frankreichs erklärt hat, dass seine Regierung grundsätzlich einer Milderung des Ausführungzwanges nicht feindlich gegenüberstehe, so kann auch mit einem Nachgeben Englands gerechnet werden, wenn gerade der Internation-

ale Kongress derjenigen Industrie, welcher in England die starken Ströme der öffentlichen Meinung gegen Beseitigung des Ausübungszwanges entsprungen sind, sich einstimmig für eine internationale Regelung durch Beseitigung des Ausübungszwanges ausspricht.

So hat auch gerade dieser Kongress in erster Linie die Legitimation, die hier behandelte Frage zu diskutieren und zu klären.

EINHEITLICHER PATENT,-MUSTER-UND MARKEN-SCHUTZ

Bericht von Verein deutscher Chemiker für den VIII. Internationalen Kongress für angewandte Chemie zu Washington und New York

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I

Man nehme nicht an, dass die Vorschläge und Tendenzen nach einer Schaffung einer einheitlichen Regelung des gewerblichen Rechtsschutzes etwa ein Ergebnis der letzten Jahre seien: im Gegenteil.

Schon auf dem ersten internationalen Kongress im Jahre 1873 in Wien auf der sogenannten Pieper-Konferenz und später im Jahre 1878 auf dem internationalen Kongress in Paris ist man überhaupt von dieser Grundlage ausgegangen. Erst als im Laufe der Verhandlungen sich ergab, dass die Erreichung dieses Ziels nicht durchführbar sei, ging man zu dem Gedanken über, die Gesetze bezw. ihre Ausgestaltung und Fortbildung den Einzelländern zu belassen und Staatsverträge aufzustellen, durch die eine gewisse internationale Regelung der Fragen angebahnt und durchgeführt werden sollte. Es lagen schon damals ganz eingehend ausgearbeitete Fragebogen für die Aufstellung eines einheitlichen Gesetzes, einer "loi type," vor und die Beratung über diese hatte eben die heute noch in Kraft bestehende, erst unlängst in Washington revidierte Pariser Uebereinkunft zum Ergebnis.

Seither sind von verschiedener Seite die Ideen wieder aufgegriffen und namentlich die Internationale Vereinigung für gewerblichen Rechtsschutz hat sich wiederholt auf ihren Kongressen mit Vereinheitlichungsgedanken befasst.

Es darf aber nicht übersehen werden, dass die Unterschiede zwischen den einzelnen Gesetzzessystemen keineswegs rein äusserlicher Natur sind. Die Eigenart der Gesetze in den einzelnen Ländern ist durch die verschiedensten Veraussetzungen beeinflusst: teils spielen historische Entwicklung eine grosse Rolle, teils Erwägungen nationaler Eigenart, was zur Folge hat, dass, wie auf allen Gebieten so auch hier sich unüberwindliche Schwierigkeiten darbieten, wenn eine völlige Ausgleichung der Gegensätze angestrebt wird. Um auf ein Beispiel auf einem anderen Gebiete hinzuweisen, sei an die seit Jahrzehnten erfolglosen Versuche einer Schaffung einer Weltsprache erinnert. Der Gedanke, eine der bereits vorhandenen Sprachen an die Stelle der übrigen zu setzen, musste als vollkommen aussichtslos längst aufgegeben werden. Aber auch der weitere Versuch, eine Kunstsprache zu schaffen, die überall Geltung haben soll kann heute getrost noch als Utopie bezeichnet werden. Nationales Selbstbewusstsein, Eifersucht auf die Erhaltung einheimischer Einrichtungen und die—vielfach nicht unberechtigte—Neigung, das für die eigene Nation beste auch beizubehalten, spielen hier zusammen, um einer Nivellierung die grössten Hindernisse zu bereiten.

Man wird daher wenigstens für die nächste Zeit mit Ausnahme der wissenschaftlichen Bestrebungen, von denen noch die Rede ist, gut tun, sich auf das Erreichbare zu beschränken, ein Weg, auf dem bereits vorwärts gegangen ist und der auch schon praktische Resultate erzielt hat.

II

Eine wissenschaftliche Untersuchung und Beratung der Unterschiede zwischen den einzelnen Erteilungssystemen und gesetzlichen Bestimmungen der einzelnen Länder ist seit Jahren in der Internationalen Vereinigung für gewerblichen Rechtsschutz angebahnt. Hier ist auf Vorschlag von Osterrieth ein sehr umfangreicher und eingehender, sorgfältig bearbeiteter Fragebogen aufgestellt. Dieser erschöpft und vertieft die Sache in jeder Beziehung. Er geht von einer geschichtlichen Betrachtung und Entwicklung der Gesetze aus, stellt dann die

allgemeinen Grundsätze, die die gegenwärtige Gesetzgebung beherrschen, auf, gibt dann im einzelnen eine Uebersicht über die Bestimmungen jedes Landes, um schliesslich in eine kritische Würdigung der Vorzüge und Nachteile jedes einzelnen Gesetzes von verschiedenen Gesichtspunkten aus einzutreten. Auf Grund dieses Fragebogens soll die Möglichkeit gegeben werden, durch eine zusammenstellende Uebersicht diejenigen Punkte festzustellen, für welche anscheinend die Möglichkeit einer internationalen Einigung besteht: ich fürchte, allzuviel solcher Punkte werden das Ergebnis der wissenschaftlichen Untersuchung nicht sein. Die gleiche Betrachtung gilt für Muster-und Markenwesen. Auch hier ist die Prüfung der Angelegenheit im Gange. Ueber den Wert einer wissenschaftlichen Abhandlung werden aber auch diese Bestrebungen nicht hinausgehen, denn auch hier sind es innere Gründe, die eine Vereinheitlichung und damit —man kann es ruhig sagen—eine Verflachung der Materie verhindern.

III

PATENTWESEN

Um eine Untersuchung über eine Vereinheitlichung dieses Gebietes vorzunehmen, ist naturgemäss notwendig, zunächst festzustellen, welche Unterschiede zwischen den Gesetzen bestehen und zwar hinsichtlich z. B. des Erteilungsverfahrens, des späteren Verfahrens, der Patentdauer, der Höhe der Patentgebühren und anderer Fragen mehr. Man wird erkennen, dass es sicherlich einzelne Bestimmungen gibt, über die eine Verständigung prinzipiell möglich ist und man wird weiter bei näherem Zusehen erkennen, dass alle diese Punkte formeller Natur sind, wie ich mich bemühen werde, darzutun.

Im grossen und ganzen kann man drei verschiedene Hauptsysteme des Erteilungsverfahrens feststellen: Anmeldeverfahren, Prüfungsverfahren und Aufgebot. Dazwischen bestehen noch verschiedene Spielarten der einzelnen Systeme. Wollte man nun dazu übergehen, eines der Systeme zur einheitlichen Durchführung für die ganze Welt vorzuschlagen, so müsste erst festgestellt werden, welches von ihnen den Vorzug verdient.

Darüber, ob die Vorprüfung, etwa wie sie zur Zeit in Amerika und Deutschland gehandhabt wird, auf die Dauer haltbar ist, sind die Meinungen bekanntlich geteilt. Andererseits bleiben aber auch noch der Zweifel genug, wenn man entscheiden will, was an die Stelle der Vorprüfung treten soll, und vor allem wird sich eines nicht für alle schicken. Länder mit entwickelter Industrie und Kultur können sich dieser Frage ganz anders gegenüberstellen, wie solche mit naivem Rechts- und technischem Verständnis. Das Gleiche gilt für die anderen grundlegenden Prinzipien der Patentgesetze. Dagegen scheint mir keine Schwierigkeit zu bestehen, um die Dauer der Patente für alle Länder gleichmässig einzurichten. Heute schwankt die Patentdauer in den einzelnen Ländern von 14–20 Jahren. Sicherlich sind bei näherer Prüfung auch diese Bestimmungen historische begründet. Aber hier möchte man meinen, es wäre ein Verlassen des Hergebrachten nicht ausgeschlossen; auch nicht für die Frage der Gebühren. Wenn auch hier fiskalische Interessen ausschlaggebend sind, deren Preisgabe man keinem Lande mit Erfolg zumuten wird, so ist es doch, objektiv betrachtet, eine Formalität, die vereinheitlicht werden kann.

Unzweifelhaft aber kann eine Uniformität durchgeführt werden, soweit es sich um äusserliche Bedingungen und Erfordernisse des Patenterteilungsverfahrens dreht. Nach dieser Richtung ist auch schon ein Anfang gemacht und auf Veranlassung eines von mir in Zürich erstatteten Berichts hat dann im Jahre 1904 eine Konferenz der Direktoren der Patentämter in Bern stattgefunden, um verschiedene Punkte einheitlich festzulegen. Hierher gehören Vorschriften wegen der Beglaubigung und Ausfertigung der Vollmacht, Vorschriften für die Formate und Anzahl der Zeichnungen, Vorschriften für die zur Inanspruchnahme der Priorität zu erforderten Papiere. Auf dieser Konferenz waren vertreten: Amerika, Belgien, Bulgarien, Dänemark, Deutschland, England, Frankreich, Italien, Japan, Luxemburg, Mexiko, Niederlande, Norwegen, Oesterreich, Portugal, Schweden, Schweiz, Tunis und Ungarn.

Die dort gefassten Beschlüsse und Wünsche sind in der Propriété Industrielle in 20. Bande vom Jahre 1904 auf Seite 162 und 163 abgedruckt, ebenfalls im Blatt für Patent-, Muster-

und Zeichenwesen vom gleichen Jahre auf Seite 355 ff. Man findet hier für Patente Bestimmungen hinsichtlich der Beschreibungen und Zeichnungen, ferner für Marken bezüglich der Bildstöcke. Auch wegen der Beglaubigung der beizubringenden Papiere sind Regeln aufgestellt und selbst bezüglich dieser an sich doch zweifellos mehr als nebenschälichen Dinge finden sich in dem Schlussprotokoll vom 5. August 1904 Proteste der verschiedenen Länder, so hat der amerikanische Vertreter erklärt, auf der amerikanischen Bestimmung wegen der Formate der Zeichnungen bestehen zu müssen, so der schwedische, es müsse zunächst bei der Vorschrift seines Landes bewenden, wonach eine Beglaubigung der begleitenden Papiere verlangt wird usw. Wenn man von diesen Formalitäten absieht und man sucht, wenig ermutigt durch die bisher erzielten Erfolge nach anderen Fragen, die einer einheitlichen Regelung zugänglich sind, so ergeben sich folgende Gesichtspunkte:

Ein weiterer Ausbau der zur Zeit bestehenden Staatsverträge, insbesondere der Pariser Konvention, ist durchzuführen, genügt aber auch, um den Bedürfnissen, die sich auf internationalem Gebiete nach der Richtung geltend machen, zu entsprechen. Hier erinnere ich an eine gleichmässige Regelung des Ausübungszwanges (Einführerverbot, Lizenzzwang).

Die Erreichung des Ziels ist auf die Weise denkbar, dass besonders abweichende Bestimmungen in den einzelnen Ländern aufgehoben werden, so dass durch eine allseitige Vereinfachung allmählich zur Vereinheitlichung übergegangen wird. Um ein Beispiel herauszugreifen, denke ich hier an die Bestimmung in Frankreich, wonach bei Uebertragung, des Patents die Gebühren für die gesamte Schutzdauer entrichtet werden müssen, eine Bestimmung, die sich nirgend wiederfindet und für deren Aufrechterhaltung sich auch kaum etwas beibringen lässt, die aber den Verkehr ausserordentlich erschwert und daher ungünstig auf die Entwicklung der Dinge in Frankreich gewirkt hat.

Die bisher gemachten Vorschläge zu einer Vereinheitlichung sind grundsätzlich zweierlei. Man hat einmal gedacht, die einmalige Anmeldung an einer Zentralstelle soll den gleichmässigen Schutz in allen Ländern gewähren. Die Undurchführbarkeit dieses Vorschlages noch weiter zu prüfen, ist wohl

überflüssig. Die Hindernisse, die sich in den Weg stellen, sind nicht nur administrative, sie sind so vielfacher Art, dass man sie überhaupt nicht weiter erörtern kann. Aber auch die etwa erhofften Vorteile können nicht eintreten. Welche unmögliche Kollision, welche Rechtsunsicherheit muss sich ergeben, wenn man sich diese Anregung Gesetz denkt.

Der zweite Vorschlag geht dahin, überall dieselben gesetzlichen Bestimmungen einzuführen. Dritte Vorschläge sind bescheidener und wünschen einen Austausch der Prüfungsergebnisse der einzelnen Länder oder den Gedanken, dass z. B. Patentvernichtung in dem einen Lande auch ohne weiteres die Vernichtung der entsprechenden Patente in den anderen Ländern nach sich ziehen soll. Alle solche Gedanken sind bestechend, sie interessieren den Menschenfreund, den Idealisten und finden immer eine Schar von Nichtpraktikern als Anhänger, ohne dadurch an Aussicht auf Erfolg zu gewinnen.

IV

MARKENWESEN

Die Bedürfnisfrage für die Marken ist ganz anders zu beurteilen, wie diejenige für die Patente, denn an diesen ist sozusagen die Industrie und die Technik nur interessiert, während an den Marken in erster Linie auch der Handel und mit den zunehmenden Verkehrsmöglichkeiten auch der internationale Handel Interesse hat. Das auf dem Gebiete der Marken bestehende internationale Abkommen, wonach eine einmalige Hinterlegung in Bern den Schutz in einer Reihe von Staaten sichert, zeigt auch den Weg, der eine Regelung der Verhältnisse ermöglicht. Zwar gehört Deutschland aus mehrfachen Erwägungen diesem Abkommen noch nicht an, auch sind ihm überhaupt noch ganz wenig Staaten beigetreten, aber ein Ausbau dieses Vertrages wird wohl den Anschluss noch weiterer Länder herbeiführen können. Darüber hinaus scheint jedes Bestreben utopisch. Was soll es aber auch für einen Zweck haben, soweit Bedürfnisse der Praxis und der Erleichterung bei der Prozedur nicht in Frage kommen. Vereinheitlichung anzustreben? Soweit die Dauer der Marken, die Gebühren, Vorschriften für die Anmeldung

von Marken etc. in Frage kommen, liegt ja alles gleich wie im Patentwesen. Ein einheitliches Gesetz aber in sämtlichen Staaten zur Geltung zu bringen, ist für Marken ebenso ausgeschlossen wie für Patente. Dagegen lässt sich hier wie dort der Grundsatz ausbilden, dass der dem Ausländer gewährte Schutz der gleiche sein solle wie der für Inländer gültige und sofern neue Schutzarten ins Auge gefasst werden, kann man auf eine gleichmässige Ausgestaltung in allen Ländern hinwirken. Hier kommt für das Markenwesen in erster Linie in Betracht die Frage der Kollektivmarken, die auch den Gegenstand eingehender Erörterung und allseitiger Zustimmung in Washington aus Anlass der diplomatischen Konferenz vom Jahre 1911 gefunden hat. Insbesondere, was hierbei die zu beobachtenden Formalitäten betrifft, kann man einheitlich vorgehen und nach dieser Richtung sind ja Bestrebungen bereits zu verzeichnen.

Für das Markenwesen kommt ferner die Erwägung in Betracht, dass schon jetzt in einer Reihe von Staaten neben dem formellen Schutz der sogenannte formlose Schutz gegen unlautere Ingebrauchnahme von Marken besteht. Auch diese Materie kann gleichmässig zu regeln versucht werden.

V

MUSTERWESEN

Es gibt die technischen Muster (Gebrauchsmuster); darüber sind besondere Gesetze nur in Deutschland und Japan vorhanden und Geschmacksmuster, die in fast allen Ländern eingeführt sind. Hier geht das Streben zunächst nach einer einheitlichen Hinterlegungsstelle, worüber der Internationalen Vereinigung schon mehrere Arbeiten geliefert sind. Mit der gleichen Einschränkung wird man hier wie bei Patenten und Marken vorgehen und auf eine gesetzliche Vereinheitlichung verzichten müssen. Aber die Formvorschriften können auch hier in gleicher Weise wie dort vereinfacht und demnächst einheitlich gestaltet werden. Dieses Gebiet des gewerblichen Rechtsschutzes interessiert auch nur einen beschränkten Kreis von Beteiligten und hat lange nicht die Bedeutung wie die beiden anderen bereits abgehandelten Gebiete.

DIE LAGE DES GEWERBLICHEN RECHTSSCHUTZES IN DEUTSCHLAND

Bericht vom Verein deutscher Chemiker für den VIII. Internationalen Kongress für angewandte Chemie zu Washington und New York

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Vor 1870 gab es in Deutschland keinen einheitlichen gewerblichen Rechtsschutz. Es bestanden nur einzelne zerstreute Gesetze; in Preussen fehlten solche gänzlich. Der Aufschwung in Industrie und Handel, der unmittelbar nach der Begründung des Reiches einsetzte, liess auch ein Bedürfnis nach einem rechtsrechtlichen Gewerbeschutz fühlbar werden. Dementsprechend entstand 1874 ein Markengesetz, 1876 ein Gesetz der Geschmacksmodelle, 1877 das Patentgesetz.

Schon nach wenigen Jahren stellte sich indessen die Notwendigkeit einer Revision des Patent- und Markengesetzes heraus. In der zweiten Hälfte der 80er Jahre setzte eine lebhafte Bewegung der Interessentenkreise ein, welche die Regierung zu einem neuen gesetzgeberischen Eingriff veranlasste. Als Folge dieser Bewegung kamen das Patentgesetz vom 7. April 1891, das Gebrauchsmustergesetz vom 1. Juni 1891, das Warenzeichen-gesetz vom 12. Mai 1894 und das Wettbewerbsgesetz vom 27. Mai 1896 zustande. Damit war die Reformbewegung bis zu einem gewissen Grade abgeschlossen.

Die nächsten Ziele der Interessenten waren auf den Ausbau des internationalen Schutzes gerichtet. Sie wurden durch den am 1. Mai 1903 erfolgten Beitritt Deutschlands zur Pariser Konvention für gewerblichen Rechtsschutz gekrönt.

Inzwischen hat sich wieder eine Bewegung nach einer neuen Reform des gewerblichen Rechtsschutzes geltend gemacht, zunächst auf dem Gebiet des jüngsten Gesetzes. Die Frucht

dieser Bestrebungen ist das neue Wettbewerbsgesetz vom 7. Juni 1909.

Eine erneute Durchsicht des Warenzeichengesetzes und des Patentgesetzes ist für die nächste Zeit von der Reichsregierung angekündigt worden.

PATENTRECHT

Das System des deutschen Patentrechts ist kurz folgendes:

Patente können erteilt werden auf neue, gewerblich verwertbare Erfindungen mit Ausnahme von Nahrungs- und Heilmittel und chemischen Stoffen. (Die Verfahren zur Herstellung dieser Stoffe sind schutzwürdig.)

Das Patent wird erteilt nicht dem Erfinder, sondern demjenigen, der die Erfindung als erster bei dem Patentamt anmeldet. Eine Ausnahme besteht nur, wenn der Anmelder dem Erfinder die Anmeldung rechtswidrig entnommen hat. Die angemeldete Erfindung wird von dem Patentamt von amtswegen und hierauf in einem Aufgebotverfahren geprüft. Die Erteilung des Patentes hat konstitutive Wirkung. Der Schutz besteht, solange das Patent in Kraft ist. Einwendungen gegen die Giltigkeit des Patentes können im Verletzungsstreit vor Gericht nicht erhoben werden, sondern nur in Form einer Nichtigkeitsklage bei dem Patentamt selbst. Das Patent kann vernichtet werden, wenn die Erfindung nicht patentfähig oder wenn sie schon Gegenstand eines früher angemeldeten Patentes war. Wegen des ersten Nichtigkeitsgrundes ist eine Vernichtung nach Ablauf von 5 Jahren von der Erteilung an ausgeschlossen.

Ausführungszwang und Lizenzzwang haben in Deutschland bestanden bis zum 1. Juli 1911. Ein Patent konnte 3 Jahre nach Erteilung zurückgenommen werden, wenn es nicht in angemessener Weise ausgeführt war, oder wenn der Patentinhaber die Erteilung von im öffentlichen Interesse liegenden Lizzenzen verweigerte. Die Einsicht, dass der Ausführungszwang den Patentschutz schwäche, führte zu dem Reichsgesetz vom 6. Juni 1911, wodurch der Ausführungszwang abgeschafft wurde. Eine Zurücknahme des Patentes kann nur noch erfolgen, wenn der Gegenstand des Patentes ausschliesslich oder vorwiegend im Auslande hergestellt wird. Ausländer können auf Grund von

Staatsverträgen hiervon befreit werden. An Stelle der Zurücknahme wegen Lizenzverweigerung ist die Möglichkeit der Erteilung einer Zwangslizenz getreten, wenn der Patentinhaber die Erteilung einer Lizenz verweigert und die Erteilung einer Zwangslizenz im öffentlichen Interesse liegt.

Der Rechtsschutz des Patentes wird durch die ordentlichen Gerichte gewährt. Die wissentliche Patentverletzung unterliegt der Strafe.

Das deutsche Patentgesetz hat sich im grossen ganzen bewährt. Der ausserordentliche Aufschwung der deutschen Industrie hat sich parallel einer ebenso gewaltigen Zunahme der Patentanmeldungen und Erteilungen entwickelt. (Im Jahre 1911 wurden 44929, also rund 45000 Patente angemeldet.) Unzweifelhaft besteht zwischen dem Patentwesen und der Entwicklung der Industrie eine Wechselwirkung: auch der Patentschutz hat zum Aufschwung der deutschen Industrie beigetragen.

Trotzdem sind schon seit Jahren gewisse Klagen in Kreisen der Patentinteressenten laut geworden, zunächst über die hohen Patentgebühren, die allerdings, von 30 Mk. im 1. Jahr bis zum Gesamtbetrage von 5300 Mk. für 15 Jahre steigend, die höchsten der Welt sind.

Ferner haben die Art und Ergebnisse der patentamtlichen Prüfung zu Klagen Anlass gegeben. Das enorme Anwachsen der Patentanmeldungen erfordert einen ausserordentlich grossen Beamtenkörper im Patentamt. Es wird die Ansicht vertreten, dass das Patentamt an der Grenze seiner Ausdehnungsfähigkeit angelangt sei, und dass infolgedessen das Verfahren einer organisatorischen Vereinfachung zu unterziehen sei, falls nicht die Qualität der Prüfung leiden und namentlich die Dauer des Prüfungsverfahrens ins Ungemessene wachsen sollte.

Ueber die Ergebnisse der Prüfung gehen die Klagen nach verschiedener Richtung. Einerseits wird beklagt, dass wertvolle und an sich patentfähige Dinge nicht zur Patentierung gelangen, andererseits wird—namentlich aus Kreisen der Industrie—Beschwerde darüber geführt, dass viel zu viel Kleinigkeiten und wertlose Dinge patentiert werden, so dass die Industrie sich überall durch innerlich wertlose Schutzrechte in ihrer Arbeit gehemmt sieht.

In neuerer Zeit haben sich in der Rechtsprechung gewisse Schwierigkeiten gezeigt, die als eine Wirkung des konstitutiven Charakters der Eintragung anzusehen sind. Durch die Erteilung des Patentes wird der Gegenstand der Erfindung von dem Patentamt in bindender Weise festgelegt auf Grund einer Prüfung, bei der naturgemäss der Stand der Technik zur Zeit der Anmeldung in Betracht zu ziehen ist. In späteren Patentverletzungssachen können naturgemäss Konflikte nach solchen Richtungen hin auftreten, die man im Zeitpunkt der Prüfung noch nicht voraussehen konnte. Daraus entsteht die Frage, wieweit der Gegenstand der Erfindung auch solchen neuen Beziehungen gegenüber festgelegt ist.

Angesichts dieser Schwierigkeiten ist angeregt worden, das System der Prüfung und konstitutiven Eintragung aufzugeben oder einzuschränken. Diese Anregungen sind aber auf starken Widerspruch bei der überwiegenden Mehrheit der Interessenten gestossen, die auf die Rechtssicherheit nicht verzichten wollen, die der jetzige Zustand ihnen zu gewähren scheint.

Die Gemüter der Interessenten sind in den letzten Jahren auch lebhaft durch die sogenannte Frage der Angestelltenerfindung beschäftigt worden. Das System der Patentgewährung an den ersten Anmelder hat zur Folge gehabt, dass man die Rechte der in industriellen Betrieben angestellten Erfinder für beeinträchtigt hält. Es ist daher angeregt worden, dem Erfinder als solchem namentlich aber dem angestellten Erfinder, einen grundsätzlichen Erstanspruch auf das Patent zu gewähren; allerdings nicht ohne Widerspruch von seiten der Industrie, die auch hier den Gesichtspunkt einer ruhigen und von inneren Streitigkeiten ungestörten Arbeitsentwicklung geltend macht.

Schliesslich ist zu erwähnen, dass eine starke Bewegung dahin geht, für die Entscheidung von Rechtsstreitigkeiten, die technische, namentlich patenttechnische Fragen, einschliessen, Sondergerichte einzuführen, in denen neben den rechtsgelehrten, auch technische Richter sitzen. Diese Bestrebungen haben begreiflicher Weise in den Kreisen der Juristen und auch bis jetzt bei den Regierungen entschiedenen Widerspruch gefunden.

Der deutsche Reichstag hat schon vor Jahren mit Rücksicht auf die Bewegung in den verschiedenen Kreisen der Interessenten

den Wunsch ausgesprochen, dass die Reichsregierung das Patentgesetz einer Reform unterziehe. Nach Mitteilungen, die der Staatssekretär des Innern vor kurzem im Reichstage machte, scheinen die Reformarbeiten schon im Werke zu sein.

GEBRAUCHSMUSTERRECHT

Neben dem Patentschutz besteht ein Schutz für kleinere Gerät erfundenen, d. h. für solche gewerbliche Neuschöpfungen oder Umformungen von Gebrauchsgegenständen, die durch ihre Neuheit dem Gebrauchszweck dienen. Solche Gebrauchsmuster können durch einfache Anmeldung beim Patentamt einen Schutz erlangen. Die Eintragung erfolgt ohne Prüfung, so dass die Eintragung nicht konstitutiv wirkt, sondern der Schutz noch von der vom Gericht jeweils nachzuprüfenden Tatsache der wirklichen Schutzfähigkeit abhängt. Der Schutz dauert zunächst 3 Jahre und kann auf 6 Jahre verlängert werden.

Die Gebühren betragen für die erste Periode 15 Mk., für die zweite Periode 60 Mk., sind also bedeutend geringer als die Patentgebühren der gleichen Schutzdauer.

Über die Schutzfähigkeit der Gebrauchsmuster hat niemals das Patentamt, sondern immer nur das Gericht zu entscheiden. Eine Löschung kann nur auf Grund gerichtlicher Klage eintreten. Auf Grund einer gerichtlichen Verurteilung wird das Gebrauchsmuster gelöscht, so dass dieses Urteil dann auch gegenüber der Allgemeinheit wirkt.

Die Leichtigkeit der Erlangung eines Schutzmittels ohne Prüfung und die Schwierigkeit der Beseitigung solcher formal bestehender Schutzrechte einerseits und die Unsicherheit eines wirklichen Schutzes andererseits haben dem Gebrauchsmuster gesetz viele Gegner erstehen lassen. Es wird darüber geklagt, dass viel zu viel Dinge, die weder neu noch nützlich sind, unter Gebrauchsmusterschutz gestellt werden; umgekehrt wird aber auch darüber Beschwerde geführt, dass gewerblich wertvolle Erfindungen, die z. B. auf dem Gebiet des Reklamewesens liegen, keinen Schutz finden können, da der Gebrauchsmusterschutz sich eben nur auf körperliche Gebrauchsgegenstände beschränkt.

Eine Reform des Gebrauchsmustergesetzes wird voraussicht-

lich gleichzeitig mit der des Patentgesetzes in Angriff genommen und durchgeführt werden.

WARENZEICHENRECHT

Der Warenzeichenschutz in Deutschland wird gegenwärtig in rein formalistischer Weise ausgeübt. Ein Schutz entsteht nur durch Eintragung beim Patentamt. Das nicht eingetragene Warenzeichen kann nur unter ganz besonderen Umständen einen Schutz finden, nämlich wenn seine Verletzung sich zugleich als eine der gesetzlich vorgesehenen Formen des unlauteren Wettbewerbs darstellt.

Die Eintragung eines Warenzeichens wird bewirkt durch Anmeldung beim Patentamt. Das angemeldete Zeichen wird einer Prüfung unterworfen und zwar nach doppelter Richtung: auf Schutzhfähigkeit und darauf, ob es nicht schon auf Grund einer früheren Anmeldung eingetragen ist.

Das Gesetz stellt für die Schutzhfähigkeit von Zeichen ganz besondere Bestimmungen auf. Ausdrücklich ausgeschlossen sind sogenannte Freizeichen, Zeichen, die ausschliesslich aus Zahlen und Buchstaben bestehen, und ferner Wortzeichen, die eine Angabe der Beschaffenheit, Bestimmung, Herkunft der Waren oder solche über Preis-, Mengen- und Gewichtsverhältnisse enthalten. Diese Aufzählung umfasst selbstverständlich alle diejenigen Zeichen, die aus irgend welchen tatsächlichen Gründen nicht unterscheidungsfähig sind. Sie wird aber in der Praxis des Patentamtes auch auf Zeichen erstreckt, die entweder ihre Unterscheidungskraft im Verkehr schon bewährt haben sehr wohl unterscheidungskräftig werden könnten, wenn man dieser Annahme nicht ausgefallene Möglichkeiten entgegenhält. Ueber die Schutzhfähigkeit entscheidet ausschliesslich das Patentamt.

Die Prüfung auf Uebereinstimmung wird zunächst ebenfalls von dem Patentamt vorgenommen. Wird eine solche festgestellt, so ergeht Mitteilung an den Besitzer des früher eingetragenen Zeichens, der daraufhin innerhalb einer bestimmten Frist Einspruch einlegen kann. Ueber diesen wieder entscheidet das Patentamt in 1. und letzter Instanz. Die Eintragung des Zeichens hat konstitutive Wirkung. Das Zeichen geniesst einen

unbedingten Schutz, solange es besteht. Es kann aber gelöscht werden und zwar von amtswegen, wenn seine Eintragung aus Versehen erfolgt ist oder auf Klage bei den ordentlichen Gerichten wegen Uebereinstimmung.

Das System und die Praxis unseres Warenzeichenrechts sind ebenfalls Gegenstand schwerer Anfechtungen von seiten beteiligter Kreise geworden. Es wird geltend gemacht, dass durch die amtliche Prüfung aller angemeldeten Zeichen (im Jahre 1911 wurden 26602 Zeichen angemeldet) dem Patentamt eine unnötige, wirtschaftlich unproduktive und auf die Dauer nicht mehr zu bewältigende Arbeitslast aufgebürdet wird. Diese Klagen führten zu dem Vorschlage, die amtliche Prüfung durch ein Aufgebotssverfahren zu ersetzen.

Ferner wird beanstandet, dass das Patentamt bei der Prüfung und Zurückweisung von Zeichen sich nicht von Bedürfnissen des Gebrauchs, sondern von philosophischen Grundsätzen leiten lässt, wodurch nützliche und für den Verkehr unentbehrliche Zeichen schutzlos bleiben. Im Zusammenhang damit ist auf den Mangel hinzuweisen, dass Zeichen, die nicht eingetragen sind, keinen oder nur einen ungenügenden Schutz geniessen. Damit steht das Warenzeichenrecht in schroffem Gegensatz zu dem neuen Wettbewerbsgesetz, das allen sonstigen geschäftlichen Kennzeichnungen, die im Verkehr bekannt geworden sind, einen Schutz gegen jede Herbeiführung einer Verwechselung sichert.

Die Erkenntnis, dass es unmöglich ist, eine solche widersprüchsvolle Gesetzgebung auf die Dauer zu erhalten, hat die Regierung schon veranlasst, die baldige Revision des Warenzeichengesetzes in Angriff zu nehmen. Es haben schon Sachverständigenberatungen stattgefunden. Man kann annehmen, dass gleichzeitig mit dem Patentgesetz oder vorher der Entwurf einer Warenzeichennovelle veröffentlicht werden wird.

WETTBEWERBSGESETZ

Das neue Wettbewerbsgesetz von 1909 sieht folgende Verbote und Schutzvorschriften vor:

1. Das Verbot unlauterer Reklame (unrichtige Angabe in

öffentlichen Ankündigungen, die geeignet sind, den Anschein eines besonders günstigen Angebots zu erwecken).

Im Zusammenhang damit wird das Ausverkaufswesen einer genauen Regelung unterworfen. Es werden Vorschriften gegeben für die Ankündigung eines Ausverkaufs (Angabe des Grundes, fakultative Vorschrift einer Anzeige bei der Polizeibehörde) und bei der Durchführung des Verkaufs (Verbot, Waren zum Zwecke eines Ausverkaufs anzuschaffen).

2. Verbot der Angestelltenbestechung (das Anbetien oder Gewähren und Fordern oder Annehmen von Zuwendungen, die den Zweck einer unlauteren Bevorzugung durch den Angestellten haben).

3. Schutz der Firma, des Namens, der Etablissementsbezeichnung, der Druckschriftentitel und aller übrigen geschäftlichen Kennzeichnungen, die im Verkehr als Kennzeichen eines Geschäfts gelten, mit Ausnahme von Warenzeichen und Warenausstattungen (§ 1 und § 15 des Warenzeichengesetzes). Der Schutz richtet sich gegen jeden Gebrauch, der geeignet ist, eine Verwechslung mit den Kennzeichnungen eines anderen herbeizuführen.

4. Schutz gegen geschäftliche üble Nachrede. Wer über ein Geschäft betriebs- oder kreditschädigende Behauptungen aufstellt oder verbreitet, muss auch deren Richtigkeit nachweisen können, widrigenfalls er auf Unterlassung und Schadenersatz in Anspruch genommen werden kann. Nur wenn diese Behauptungen vertraulicherweise aus berechtigtem Interesse mitgeteilt werden, liegt der Beweis der Unrichtigkeit der Behauptung dem Betroffenen ob. Schadenersatz ist im Falle von Vorsatz und Fahrlässigkeit gegeben, Strafe im Falle wissentlichen Handelns.

5. Den Schutz der Geschäfts- und Betriebsgeheimnisse.

a) Alle Angestellten sind während ihres Dienstverhältnisses verpflichtet, die Geheimnisse des Betriebes oder Geschäfts zu bewahren, d. h. nicht selbst gewerblich zu verwerten oder anderen zu Zwecken des Wettbewerbs mitzuteilen.

b) Niemand darf fremde Geschäfts- oder Betriebsgeheimnisse, die er durch Untreue eines Angestellten oder eine unlautere Handlung erworben hat, zu Zwecken des Wettbewerbes selbst verwerten oder an andere mitteilen.

c) Wer einem Anderen im geschäftlichen Verkehr technische Vorlagen und technische und andere Entwürfe, Vorlagen, Rezepte usw. vertraulich mitteilt, ist dagegen geschützt, dass diese Vorlagen zu Zwecken des Wettbewerbs Dritten mitgeteilt oder verwertet werden.

d) Auch die Anstiftung zum Geheimnisverrat ist verboten. (Das Zu widerhandeln gegen sämtliche Vorschriften unterliegt strenger Strafe.)

6. Schliesslich stellt das Gesetz in der Generalklausel des § 1 das allgemeine Verbot auf, im geschäftlichen Verkehr zu Zwecken des Wettbewerbs Handlungen zu begehen, die gegen die guten Sitten verstossen, bei Vermeidung einer Unterlassungs- und Schadensersatzklage. Durch diese Generalklausel können alle Fälle des unlauteren Wettbewerbs getroffen werden, die gegen das sittliche Empfinden des anständigen Geschäftsmanns verstossen ohne Rücksicht darauf, ob sie unter einen besonders geregelten gesetzlichen Tatbestand fallen oder nicht.

Bemerkenswert ist noch, dass bei den Verbotsvorschriften nicht nur die persönlich Geschädigten eine Unterlassungsklage anstrengen können, sondern alle Konkurrenten und auch gewerbliche Verbände mit juristischer Persönlichkeit. Damit ist dem einzelnen Geschäftsmann ein weitreichendes Kontrollrecht gegenüber seinen Gewerbegenossen gegeben.

Das Wettbewerbsgesetz von 1909 hat im grossen ganzen befriedigend gewirkt. Besonders hat die Anwendung der Generalklausel die Gerichte zu einer freien Beurteilung der Verkehrsverhältnisse geführt und auch in den Geschäftskreisen selbst das Unterscheidungsvermögen für zulässige und unzulässige Handlungen geschärft. Es ist anzunehmen, dass das gegenwärtige Gesetz eine Reihe von Jahren ohne wesentliche Änderung bestehen wird.

INTERNATIONALER RECHTSSCHUTZ

Deutschland gehört seit 1903 der Pariser Konvention an, dagegen nicht den beiden Madrider Abkommen.—Ausserdem hat Deutschland mit der Schweiz, Italien und den Vereinigten Staaten Sonderverträge abgeschlossen, durch welche der Ausführungszwang in den Beziehungen zwischen Deutschland und jedem dieser Länder praktisch beseitigt ist.

DAS PRIORITÄTSRECHT DER PARISER KONVENTION

Bericht vom Verein deutscher Chemiker für den VIII. Internationalen Kongress für angewandte Chemie zu Washington und New York

RECHTSANWALT DR. M. WASSERMANN
Hamburg, Germany

Die wichtigste Voraussetzung eines gütigen Patents ist die Neuheit der Erfindung. In diesem Punkte stimmen die Patentgesetze aller Länder überein; lediglich darin unterscheiden sie sich, ob die Prüfung der Neuheit vor Erteilung des Patentes durch die mit der Patentierung betraute Behörde geschieht, oder ob sie nach Bewilligung es Patentes in Form einer gerichtlichen Nachprüfung erfolgt.

Als kritischer Zeitpunkt für die Neuheitsprüfung gilt überall der Tag, an welchem der Patentschutz nachgesucht wird. Ereignisse, die später eintreten, insbesondere Veröffentlichungen und Benutzung der Erfindung innerhalb des zwischen der Anmeldung und Erteilung des Patentes liegenden Zeitraums sind einflusslos, sie haben keine neuheitszerstörende Wirkung.

Derjenige, der sich einen gütigen Patentschutz für seine Erfindungen in mehreren Staaten sichern will, muss daher dafür sorgen, dass die Anmeldung in allen diesen Ländern so früh wie möglich erfolgt, da jeder Tag der Verzögerung die Gefahr eines neuheitszerstörenden Aktes mit sich bringt.

Die Anmeldung eines Patentes kostet Geld, in einem Lande mehr, in dem andern weniger; in keinem Lande ist sie unentgeltlich. Bei der Anmeldung im Auslande kommt zu den eigentlichen behördlichen Gebühren noch die Kosten für Uebersetzungen und das Honorar für den im Auslande nicht zu entbehrenden Patentanwalt oder sonstigen Vertreter hinzu. Da nun Erfinder sehr reich an Ideen, aber desto weniger gesegnet mit irdischen Schätzen zu sein pflegen, so reichen ihre

verfügbarer Mittel oft nicht aus, um die mit einer gleichzeitigen Patentanmeldung in mehreren Ländern verbundenen Spesen aufzubringen, und da sich kapitalkräftige Interessenten an der Ausbeutung einer Erfindung in der Regel erst dann beteiligen, wenn ein Patent erteilt oder doch in ziemlich sichere Aussicht gestellt ist, so ist der finanziell schwache Erfinder oft genötigt, auf den Patentschutz im Auslande zu verzichten.

Abhilfe gegen diesen für den Einzelnen wie für die Industrie schädlichen Zustand schafft die im Jahre 1883 von einer Reihe von Staaten in Paris geschlossene Internationale Uebereinkunft, die sogenannte Pariser Konvention, der die Vereinigten Staaten seit 1901, das Deutsche Reich seit 1903 angehören. Durch ihren Art. 4 ermöglicht sie es dem Erfinder durch die Anmeldung der Erfindung in *einem* der Verbandsstaaten sich die Priorität in allen übrigen für 12 Monate zu sichern. Sucht er innerhalb dieses Zeitraumes ein Patent auf die gleiche Erfindung auch nur in einem oder mehreren anderen Unionsländern nach, so wird er dort hinsichtlich der Neuheit so behandelt, als ob das Gesuch am Tage der ersten Anmeldung eingereicht wäre. Ein während dieser 12 Monate eingetretenes Ereignis hat mithin keine neuheitszerstörende Wirkung.

Diese Bestimmung ist von ungemein grosser praktischer Wichtigkeit für den Erfinder; sie ermöglicht es ihm, durch die relativ billige Anmeldung in *einem* Lande sich ein volles Jahr die Aussichten gültiger Patente in allen übrigen Unionsländern zu sichern. Ohne dass das Damoklesschwert neuheitszerstörender Ereignisse über seinem Haupte schwebt, kann er in diesen 12 Monaten prüfen und prüfen lassen, ob und welche Aussichten auf gültige Patentierung er hat. Fällt die Prüfung ungünstig aus, kann er die Kosten für die Auslandspatente sparen; ergibt sie ein günstiges Resultat, so findet er jedenfalls leichter die Unterstützung eines Kapitalisten. Unter Umständen wird er selbst auch innerhalb 12 Monaten eher in der Lage sein, die Mittel für die Auslandspatente aufzubringen, als wenn er dies gleich bei der ersten Anmeldung hätte tun müssen.

Man kann daher ohne Uebertreibung sagen, dass durch die Pariser Uebereinkunft die Erlangung des Patenschutzes im Auslande wesentlich erleichtert worden ist. Diese Vorteile

geniessen nicht nur alle Staatsangehörige eines Verbandslandes, sondern nach Art. 3 auch die Untertanen und Bürger eines dem Verbande nicht beigetretenen Staates, welche in einem der Verbandsstaaten ihren Wohnsitz oder eine (tatsächliche und wirkliche) gewerbliche oder Handelsniederlassung haben.

Obwohl also beispielsweise China der Union nicht angehört, hat der Chinese, der in den Vereinigten Staaten wohnt oder ein Geschäft betreibt, Anspruch auf den Schutz des Art. 4. Wenn er eine Erfindung hier oder in Frankreich, Belgien, England usw. zum Patent anmeldet, so wird er bei einer eventuellen späteren Anmeldung in Deutschland, Italien, Oesterreich, usw. bezüglich der Priorität ebenso behandelt, wie der Bürger der Vereinigten Staaten.

Da bekanntlich der Schutz eines Patentes ein zeitlich beschränkter ist—er beträgt in den meisten Ländern 15, in den Vereinigten Staaten 17 Jahre—, so ergibt sich aus der soeben behandelten Bestimmung die für den Erfinder wichtige Frage, ob bei einem sich auf Unionspriorität stützenden Patent das *Datum der ersten (Stamm-)Anmeldung* für die *Lebensdauer* der später in den anderen Unionsstaaten genommenen Patente massgebend sei, oder ob diese letzteren erst vom Tage ihrer eigenen Anmeldung an gerechnet werden sollen.

Der Art. 4b der Pariser Uebereinkunft bestimmt allerdings, dass die in den verschiedenen Unionsstaaten genommenen Patente von einander unabhängig sein sollen, und in Deutschland wird Art. 4b auch dahin ausgelegt, dass die Prioritätsfrist für die Lebensdauer der in Deutschland mit ausländischer Priorität genommenen Patente nicht mitzählt, sondern der deutsche Anmeldungstag als Geburtstag gilt. Diese Auffassung wird jedoch nicht von allen übrigen Unionsstaaten geteilt; manche datieren vielmehr die Geburt auf den Tag der ersten Anmeldung zurück und verkürzen so das Leben des Patents unter Umständen um volle 12 Monate.

Diese Praxis galt vor 1898 in den Vereinigten Staaten; seit dieser Zeit ist sie jedoch aufgegeben. Ein heute in den Vereinigten Staaten angemeldetes Patent läuft volle 17 Jahre, selbst wenn es etwa auf Grund einer früheren Anmeldung in England eine Priorität vom September 1911 in Anspruch nimmt.

In Belgien, Italien und England wird dagegen noch heute das Patent auf den Tag der ausländischen Stammanmeldung zurückdatiert; auf der vorjährigen Konferenz in Washington machten Deutschland und Frankreich den Versuch, durch einen Zusatz zu Art. 4b diese Verschiedenheit zu beseitigen und die heute in Frankreich, Deutschland und Amerika geltende Methode in allen Unionsstaaten bindend vorzuschreiben; dieser Versuch scheiterte jedoch an dem Widerstande Englands—wenigstens vorläufig noch (Osterrieth in G. R. u. U. 1912 S. 10). Sie übrigen Unionsstaaten standen, selbst soweit sie diese Praxis nicht selbst befolgen, dem Vorschlage sympathisch gegenüber. Man darf deshalb wohl erwarten, dass über kurz oder lang in diesem Punkte eine einheitliche Regelung erfolgen wird.

Eine weitere Frage von praktischer Bedeutung ist, in welcher *Form* und in welchem *Zeitpunkt* die *Priorität geltend* gemacht werden muss.

Die Handhabung in den verschiedenen Verbändsländern ist in dieser Hinsicht keine einheitliche; in einigen Staaten werden dem Anmelder recht unbequeme Formalitäten auferlegt, deren Beseitigung die internationale Vereinigung für gewerblichen Rechtsschutz seit Jahren in Wort und Schrift gefordert hat. Die Behörden anderer Staaten, z. B. das deutsche Patentamt sind äusserst liberal; sie überlassen es dem Anmelder vollständig, ob, wann und in welcher Form er seine etwaige ausländische Priorität geltend zu machen für gut befindet; nur sachlich ist in Deutschland die Geltendmachung des Prioritätsrechts insofern beschränkt als bei der Anmeldung der Erfindung in *mehreren ausländischen* Staaten nur die *älteste Anmeldung* eine *Priorität begründet* (Blatt für Patent-, Muster- und Zeichwesen 1908 S. 109, S. 180; 1910 S. 135). Das formlose deutsche Verfahren hat allgemeinen Beifall gefunden. Demgemäß wurde auf der vorjährigen Konferenz der Unionsstaaten zu Washington beschlossen, in allen Ländern die Formvorschriften auf ein Minimum zu reduzieren. Der in diesem Sinne ergänzte Art. 4—der natürlich erst mit der Ratifikation der Washingtoner Beschlüsse Gesetzeskraft erlangt—bestimmt:

1. Wer eine Priorität beansprucht, muss dies erklären und das Land und Datum der betreffenden Anmeldung angeben.

Hierdurch sollen die Interessenten, auch die des Auslandes, auf die Tatsache eines Prioritätsanspruchs aufmerksam gemacht werden (Osterrieth in G. R. u. U. 1912 S. 7).

2. Jedes Land bestimmt, bis zu welchem Zeitpunkt spätestens diese Erklärung abgegeben werden muss.

Es versteht sich von selbst, dass der Zeitpunkt vor der Veröffentlichung liegen muss; denn auf allen Veröffentlichungen—insbesondere auf dem Patent selbst—is diese Angabe zu erwähnen.

Im übrigen schreibt der Art. 4 in seiner neuen Fassung vor, dass die Patentämter bei Geltendmachung einer ausländischen Priorität die Vorlage einer Abschrift der früheren Anmeldung (Beschreibung, Zeichnung, etc.), ein Zeugnis über das Datum desselben und eine Uebersetzung verlangen können. Beglaubigung durch die zuständige Behörde genügt; Legalisation ist nicht nötig. Weitere Formalitäten soll kein Staat zum Nachweis der Priorität bei der Anmeldung verlangen dürfen.

Durch dieses in Washington beschlossene *Höchstmass der Formvorschriften* wird also in Zukunft die Geltendmachung der Priorität im Bereich der Pariser Union zum Teil wesentlich vereinfacht werden.

Es kann nicht die Aufgabe dieser durch die Kongressleitung zeitlich sehr begrenzten Betrachtung sein, auf die zum Teil hoch interessanten Rechtsfragen einzugehen, die sich an die Auslegung der Art. 4 und 4b der Uebereinkunft geknüpft haben, und die vielen Wünsche zu erörtern, die auch durch die Washingtoner Konferenz nicht erfüllt sind; ich muss mich vielmehr darauf beschränken, zum Schlusse einen Punkt hervorzuheben, in welchem der jetzige Zustand dringend reformbedürftig ist, nämlich die Dauer der *Prioritätsfrist für Fabrik- und Handelsmarken*. Ich habe bisher der Einfachheit halber nur von Patenten gesprochen und deshalb nur die 12 monatliche Prioritätsfrist erwähnt. Das Prioritätsrecht der Union beschränkt sich jedoch nicht auf Patente, sondern erstreckt sich in gleicher Weise auf *Gebrauchsmuster, Geschmacksmuster* und auf *Fabrik- und Handelsmarken*.

Die Gebrauchsmuster spielen im internationalen Verkehr keine grosse Rolle, da es solche nur in Deutschland und Japan gibt;

sie sind in dem neuen Art. 4 bezüglich der Prioritätsfrist den Patenten gleichgestellt.

Die Geschmacksmuster dürften für den hier versammelten Kreis keine besondere Bedeutung haben; erhebliches Interesse bieten dagegen die *Fabrik- und Handelsmarken*, deren sich die chemische Industrie in hohem Masse bedient, und die dazu bestimmt sind, ihren Produkten nicht nur in der Heimat, sondern im grossen internationalen Verkehr Schutz gegen Nachahmung zu sichern. Ich brauche Sie nicht an die weltbekannten Marken amerikanischer, englischer und deutscher chemischer Fabriken zu erinnern deren Wert Millionen repräsentiert; ohne sie würde die chemische Industrie heute überhaupt nicht auskommen können.

Der Art. 4 der Pariser Konvention gewährt auch dem Anmelder einer Marke ein Prioritätsrecht in dem Sinne, dass die Anmeldung in *einem* Unionsstaate während gewisser Frist dem Anmeldenden einen Vorrang in den übrigen Ländern gewährt, genau wie bei einem Patente, nur mit dem Unterschied, dass die Frist nicht 12, sondern nur 4 Monate beträgt. Diese Frist genügt in solchen Ländern, in denen die Registrierung der Marke ohne irgend welche zeitraubende Prüfung erfolgt; dagegen ist sie viel zu gering für diejenigen Staaten, in denen der Eintragung eine behördliche Prüfung vorangeht, wie z. B. Deutschland, Oesterreich usw.; denn nur ein verschwindend kleiner Prozentsatz der in diesen Staaten angemeldeten Warenzeichen wird innerhalb dieser Frist eingetragen.

Der Vorschlag der deutschen Regierung, die Prioritätsfrist für Marken auf 12 Monate zu erweitern, wurde jedoch leider auf der Washingtoner Konferenz abgelehnt.

(*Abstract*)

THE MOVEMENT FOR CONSERVATION OF NATURAL GAS IN THE UNITED STATES

RALPH ARNOLD AND FREDERICK G. CLAPP

Natural gas occurs in commercial quantities in twenty-three States of the United States. In 1910 there were produced 509,155,309,000 cubic feet of it, having a total value of \$70,756,158. The estimated area of gas fields in the country is 9,365 square miles. The seven principal regions are the Appalachian, Ohio-Indiana, Central Ohio, Kansas-Oklahoma, Louisiana, Texas and California. Gas was first utilized in the United States at Fredonia, New York, in 1821. The intensive development of the industry in Pennsylvania began about 1876, and was followed by development in Ohio in 1884, in California in 1890, in Kansas in 1894, in Texas in 1901, and in Oklahoma and Louisiana in 1905.

Previous to 1873 there was little waste of gas, but beginning with that year, and practically up to the present time, the annual waste has been appalling. For years it was the belief that the supply was inexhaustible, but with the decline of some fields and absolute failure of others, the fact was brought home to the American people that if remedial measures were not taken the supply would soon be gone. Thanks to the foresight and energy of many of the operators the waste has been materially reduced or practically stopped in most of the fields, and it may now be said that with the exception of certain new wells, control of which has not been gained, there is little wholesale waste of gas.

The principal avenues through which natural gas is wasted may be summarized as follows:

- (a) Waste in drilling and casing wells.
- (b) Waste from high pressure wells.
- (c) Waste in oil production.

- (d) Waste owing to lack of proper care of wells.
- (e) Waste in transportation.
- (f) Waste in utilization.
- (g) Waste owing to improper plugging.

The principal waste has naturally been in connection with wild wells, cases of a loss of from 50,000,000 to 75,000,000 cubic feet per day being known from single wells. Instances of losses aggregating \$1,000,000 to \$3,000,000 from single wells have been recorded from various fields. The total daily loss from individual States has run as high as 500,000,000 cubic feet. The next most important source of waste, and one which can easily be remedied, is in connection with oil production. The waste from the sale of gas by what is called a "flat rate" or without measuring it through meters, is another not unimportant source that can be easily closed. The decline of fields owing to waste or improper utilization has been most marked, and is more than anything else, what has led to the conservation movement.

Several of the States have already passed laws restricting the waste of gas, and other States are seriously considering the question. The matter of gas conservation has also been one of the chief topics at the conservation conferences and conventions. Among the men who have been instrumental in bringing the subject before the people might be mentioned J. C. White, State Geologist of West Virginia; J. C. McDowell, Dr. Orton, Dr. Joseph A. Holmes, and others. One of the best definitions of conservation which can be appropriately applied to the conservation of natural gas is that by Dr. C. W. Hayes, formerly Chief Geologist of the U. S. Geological Survey, who says: "Conservation is utilization with a maximum efficiency and a minimum waste."

The importance of conserving natural gas may be summarized as follows:

1. Natural gas is the cheapest, cleanest, most easily controlled and best fuel known to civilization.
2. Its discovery is usually immediately followed by utilization.
3. Large amounts of money have been spent in installing gas pipe lines.
4. Large amounts of money have been invested in industrial

enterprises in the vicinity of gas fields, and are in many cases, absolutely dependent for their existence on the gas supply.

5. Towns have grown up surrounding these industrial plants, and are thus indirectly dependent on the cheap fuel.

6. Towns in the vicinity of gas fields have become dependent on this fuel, and a failure of the supply would necessitate costly changes in heating and fuel arrangements or an abandonment of the town.

7. The present cost of gas for domestic purposes is much less than that of other available fuel, and its use much more convenient.

8. Nearly every town in the gas fields has increased its population due to the discovery of gas; this excess population would be largely lost with a failure of the gas supply.

9. The wealth and revenues of all states and communities where gas exists is greatly augmented by the presence of the gas supply.

10. Large numbers of public institutions have been equipped for the use of gas, and the failure of the supply would entail a large expenditure of public funds for alterations necessitated by the change of fuel.

11. If the supply can be conserved the cities and industries will continue to grow instead of decline, as would be the case if the gas failed.

12. In a broad economic sense, every cubic foot of gas wasted is an absolute loss for the substance can never be regained; neither does it serve any useful purpose when dissipated in the air.

13. In addition to the absolute loss of the escaped gas, there is the resultant loss of pressure rendering the remaining gas less available.

14. In some arid regions, particularly California and Texas, except for oil, gas is the only resource of certain areas, and for that reason should be doubly safeguarded.

15. The question of gas conservation is directly connected with the conservation of coal and the saving of human lives in the coal mines, for the reason that if the gas is permitted to leak from old or improperly cased wells which penetrate workable

beds of coal, disastrous explosions are liable to occur from the escaped gas.

The following means have been proposed for conserving the natural gas supply:

1. Precautions in drilling and casing wells.
2. Saving gas from oil wells.
3. Controlling and capping wild wells.
4. Proper care of the wells.
5. Proper utilization of natural gas.
6. Improved legislation on the subject.
7. Improved methods of consumption.
8. Prevention of leakages.
9. Increase in gas rates.
10. Use of meter system.

Aside from the actual prevention of waste, one of the best methods of conserving the supply of gas is found in utilizing it in internal combustion or gas engines rather than in the production of steam. The efficiency of the best type of gas engine as compared with the ordinary steam engine with gas as a fuel for steam generation, is as 10 up to 14 is to one.

WHAT THE UNITED STATES IS DOING TOWARD THE CONSERVATION AND IMPROVEMENT OF SOIL FERTILITY

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SOIL MANAGEMENT

Conservation of Soil Fertility as a practical matter consists in the judicious management of the soil so as to obtain large (but not necessarily maximum) crops and at the same time, render the soil capable of continuing to yield as large or larger crops. The instrumentations of soil management fall under the three heads of tillage, crop rotations and fertilizers, all of which have long been known. But to use these instrumentations intelligently and in the spirit of the conservation ideal it is necessary to understand the soil, the materials composing it and the processes taking place therein.

THE MODERN VIEWPOINT

The tendency of recent investigations is to establish a new viewpoint the chief characteristics of which may be summarized as (1) All the factors in a soil which influence crop production involve more or less continuous movements or states of change, (2) All the factors in a soil which influence crop production are mutually interdependent, i.e., one cannot be affected without corresponding effects on the others and the general resultant, and (3) Soils are individuals, i.e., mixtures of such complexity that no two are or can be made exactly alike in crop producing powers or response to cultural treatments.

SOIL SURVEY

Individuals can be classified and must be for systematic investigation. Hence, the Soil Survey classifies soils into *types*, the types falling into *series* and the series naturally grouping themselves into *provinces*, the soil provinces corresponding fairly closely with the great physiographic provinces. This suggests at once that origin of material is a basic factor and that the classification is essentially a genetic one, and the experience of the world has shown that genetic classifications are the most useful and consequently the ones which persist. Essentially though not professedly the classification employed by the Soil Survey is a genetic one, the primary consideration being the obvious physical characteristics such as texture and color, the mineralogical, chemical and biological characteristics being subordinated but by no means neglected.

SOIL PHYSICS

The physical properties of soils, especially their textural characteristics are receiving especial attention. It has been shown that nearly if not quite every physical property of the soil affecting crop production is a function of the water content of the soil, and the water holding power of the soil is determined by the texture, that is by the relative sizes and arrangements of the particles composing the soil. The texture is more or less affected by tillage operations, by crop rotations as in alternation of deep and shallow rooted plants, by fertilizers both organic and mineral. Consequently all these agencies affect the content and movement of water in the soil and its relation to plant growth.

The water in a soil may be divided into two classes, that which is adhering to the soil grains and floccules in films, and the free water of the interstitial spaces. The soil is in the best physical condition for plant growth when it contains as much film water as possible, without any free water. This "critical moisture" or "optimum moisture" content is a definite characteristic for each particular soil, and is higher, generally, the finer the texture

of the soil. Hence texture is more easily correlated than any other factor with suitability for the growth of particular plants, groups of plants or rotations. Texture is not alone the determining factor however, as witness the oft quoted fact that in the humid areas of the United States, heavy soils are preferred for wheat and in the semi-arid areas a light or sandy soil is preferred. With the growing appreciation of the importance of the mechanics of the soil, and soil movements these subjects are receiving especial attention in federal investigations at the present time, especially translocation and local movements of the solid particles and the distribution of rainfall and movements of the soil solution.

SOIL WATERS

Soil Water Investigations are in progress to determine the effects of a man's occupation of the surface upon the storage and movements of this most important material for plant production and indeed of every form of life. An enormous mass of material has been accumulated showing that the "settling up" of the country has been accompanied, generally, by a lowering of the water table or ground water level. And the control of this water level, the economic storage in the soil of the greatest possible amount of the annual precipitation, the translocation and local movements, the relation of soil moisture to cultural treatments, atmospheric movements, etc., with a view to control and management, is now being studied. Closely related in a practical way are studies of soil erosion on the one hand and "dry farming" on the other.

SOIL SOLUTION

Especial consideration has been given to the distribution of the rainfall and more especially to that part, normally two thirds or over, which penetrates the upper soil, to return to the surface later as capillary or film water and constituting the soil solution. The concentration and composition of the soil solution, the great natural culture medium for plants, its relation to the soil atmosphere, to the solid mineral complex and the

even more complex of organic débris known popularly as humus, has been studied assiduously as giving perhaps the best possible point of attack upon the complicated relations between soils and growing plants. Not only has the normal supply of mineral plant nutrients received attention but the specific properties of a number of organic components have been studied as they affect plant growth and as their effects are modified by the common components of manures and fertilizers.

MINERAL COMPOSITION

It has long been assumed that but few inorganic constituents of a soil are of any importance in determining its crop producing power or "fertility." This notion has been much questioned in the past few years. But as a result very little has been done in the way of determining the composition of soils in anything approaching a complete or comprehensive way. Consequently investigations are now actively in progress to determine what are the minerals or combinations in our typical agricultural soils and at the same time careful quantitative investigations are being made of the composition for each and every constituent for which analytical methods exist. No such inventory of soils has ever before been attempted, and the results of this investigation are expected to be of unusual value for future investigations.

ORGANIC CONSTITUENTS

Until quite recently the organic debris forming a relatively small but important part of the soil, has been a mysterious *terra incognita*, designated usually as "humus" and assumed on very unsatisfactory evidence, to be a mixture of various complex but indefinite acids,—humic, crenic, apocrenic, ulmic, etc. Within the past few years, and mainly in federal investigations, the composition of humus has been rationally investigated and upwards of 30 definite, well characterized organic compounds have been isolated from soils, identified and their properties noted. Some of these have been found to benefit plants by

their presence, others have been found harmful, and still others practically of no effect. The action of the harmful or "toxic" substances can be modified by various cultural agencies and notably by the inorganic constituents of commercial fertilizers. The origin and genesis of the organic degradation and decomposition products, whether direct resultants of plant metabolism (root excreta, etc) or of secondary processes within the soil, is generally quite obscure, but is being investigated as of fundamental importance not only to a knowledge of the soil's properties but to its technical management.

BIOLOGICAL PROPERTIES

Besides the examination of the soil to determine the nature of the organic constituents and the origin and genesis of these constituents, the biological processes taking place in the soil are receiving some general consideration. The major attention in federal investigations however has been concentrated on the control, within the soil, of azo-bacteria and especially the varieties growing in symbiosis with leguminous plants, and their dissemination artificially.

ROTATIONS

No instrumentation of soil control is more important than crop rotation. The problem is however always much modified not only by technical soil and plant considerations but by market, transportation, economic and social factors. Consequently so far as federal work in this direction is concerned it has been along "practical" rather than "theoretical" lines. The determination of suitable rotations has been and is an important integral part of the federal work on Farm Management, and under the caption, diversified farming, has been the basis of the farm demonstration work notably successful under the guidance of the late Dr. Seaman A. Knapp in improving conditions in the Southern States.

FERTILIZERS

While the theory and practice of the instrumentations of soil management have all received consideration in federal investigations, recently, special attention has been given to fertilizers. Three distinct problems are presented which can be grouped under: (1) Supplies of raw material; (2) Factory manipulation, and distribution or sale; and (3) The use of fertilizers. Of these but little has been done by the federal government on (2) and the scope of the main work on (3) has been outlined above. As regards (1) it has been shown that the United States is unique in possessing ample supplies for an indefinite period into the future. But that these shall be employed to the best advantage of the community as a whole it is imperative that the conservation ideal be insisted upon immediately and strenuously. Enormous wastes are now going on.

An ample supply of potash salts, larger than our present needs and probably competent to meet any future requirements can be annually obtained from the giant kelps of the Pacific littoral if the natural groves are protected and harvested conservatively. Supplemental supplies of potash can be obtained from certain known lakes or deposits, and of these several seem to have possible economic value in the near future. The extraction of potash from feldspar, leucite and similar natural silicates, has long been a dream of applied chemistry and several processes of possible commercial importance are now being exploited. It has been shown on an experimental scale that ground feldspar, substituted for clay would probably make a desirable cement clinker, and at the temperature of the furnace there is practically quantitative separation of potash which can be trapped with the flue dust. Alunite has been shown to be an important if minor possible source of potash.

The phosphate deposits of the Charleston area appear to be waning, and the end of the hard rock of Florida is thought by many to be in sight. But new deposits of pebble phosphates are continually coming to light, and it has recently been demonstrated that if the Tennessee phosphates are mined in accordance

with conservation ideals they have many years of productivity ahead. Arkansas, Kentucky, and possibly other localities may yet prove important phosphate fields, but the recently described phosphate deposits of Utah, Wyoming, Montana, and Idaho are known to contain enough high grade material to supply demands for more than a decade of centuries. As time goes on and knowledge of our territory increases it becomes less probable that any natural deposits of nitrates of economic importance will be found. Artificial nitre beds are probably impossible for American conditions. If all coking were done in by-product ovens as should be the case an important but totally inadequate supply of nitrogen as ammonium salts would become available. Cotton seed meal, dried blood, tankage, garbage and possibly other city wastes if garnered and handled in accordance with the true "conservation spirit" will materially assist in the nitrogen problem. The increase in intensive cultivation with the employment of a leguminous crop in the rotation will undoubtedly be a major factor in meeting the nitrogen problem for general field crops. But we have practically unlimited supplies of both limestone and atmospheric nitrogen and with sufficiently cheap power calcium cyanamid and basic calcium nitrate or possibly other nitrogen carriers may well become dominant factors in American agriculture and the nation's welfare. This seems to be a point worthy of more attention by the propagandists of the Conservation Movement than it has yet received.

USE OF SOILS

The soil may be abused to such extent that it does not respond economically in crop production to ordinary management. In common parlance it is "worn out." It does not become, however, lost in the list of national assets as with burnt coal. Always, by methods which may or may not prove tedious and expensive, it can be restored to productivity and when thus restored it can be maintained, usually quite readily. But soils as pointed out above are individuals with particular adaptabilities, capabilities for particular crops or rotations, and responsiveness to cultural methods, although these soil individuals are also capable

of being classified into groups. No more important single example of practical conservation work can be cited than the federal government's work in gathering together the results of investigation and pointing out in a series of publications for practical farmers, the crop adaptations, and other uses, and the cultural needs of the important soil types thus far recognized. We can point with justifiable pride to the importance, amount and economic value of this work. But we should at the same time maintain a certain humility of spirit because applied science and especially applied chemistry is playing a far less important part than it should in guiding one of the great national movements now in progress, namely, the transition from pioneer or extensive farming to settled or intensive farming. The federal government and applied chemistry, in different ways and yet alike, are servants of the people; no matter what or how great their past achievements they should ever be expected and required to do far more to justify their continued existence.

(*Abstract*)

PEAT AS FUEL

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Reports of the growing use of peat as fuel in Europe have stimulated the interest of owners of peat land in the United States especially in those parts of the country where other fuels are high in price; and many attempts have been made to make peat fuel on a commercial scale in this country, so far without success.

A careful analysis of the reasons for this failure however shows that not the peat, but easily remedied causes, largely due to ignorance and inexperience, were responsible for the failures. Such peat fuel as has been produced has always been sold readily at satisfactory prices. It, therefore, seems worth while to examine into the possibilities of peat as fuel and learn if it may not have a place as an auxiliary fuel, at least, in the parts of the country where it is found to relieve those consumers who are remote from coal mines from the high prices to which other fuels now command.

Upwards of 15,000,000 tons of peat fuel are produced and used annually in Europe and its use for the production of steam and electric power is noticeably increasing in countries where peat is abundant, although as heretofore the great part of the peat fuel is used for domestic consumption.

In the United States peat is found in abundance in the region north of the Ohio River and east of the 100th Meridian. It also occurs in New York and New England and along the Atlantic Coastal plain to Florida which has large peat deposits and on the Pacific Coast in California, Oregon, and Washington. It will be seen that this distribution is such that the peat deposits are almost entirely in States with little or no coal.

The chief characteristic of peat which makes its production for fuel difficult is it always contains a high water content, from 85 to 90 per cent., which must be removed before the peat can be burned. All processes for preparing peat fuel are based on attempts to remove the water cheaply and certainly. They are made difficult by the fibrous and woody material of which the peat is composed and by the peculiar water-holding power of the organic chemical compounds present. The water mixed with the peat cannot be removed from masses of the solid materials either by pressure or by centrifugal force below about 70 per cent.

Commercial methods of producing peat fuel are limited at the present time to those which depend, in large part, at least, on drying the peat by exposure to the air. A few cases are reported where the peat is partly air-dried and the moisture farther reduced by the use of artificial heat. The greater part of the peat fuel made and used in Europe is in the form of air-dried bricks or blocks which have been either cut from the bog with special spade like tools, or been formed by machines which first grind or macerate the wet peat to a pulp and then form it into bricks as it issues from the machines. Some processes spread the pulp on the surface of a drying ground in a thin sheet and form the bricks by marking the sheet with properly spaced markers. When partly dried the peat is turned by hand labor, then piled in small heaps for a time, and finally stacked till used; the product is called machine peat. Recently devised machines seem likely to eliminate most of the hand labor from the methods now in use abroad for making machine peat, and thus do away with one important objection to its use in the United States. Air dried machine peat is the kind of peat fuel used in power and industrial works in Europe, with very few exceptions.

Briquetting peat has been tried in many countries and the most notable failures at peat fuel production in the United States have been of plants of this kind. At present peat briquets are made in but very few places in Europe, and the quantity produced is small. A much larger and more costly plant is needed to make briquets than is required for air-dried machine peat, and more money is required to run it.

Peat charcoal or coke. Machine peat may be coked in proper retorts and wood alcohol, acetic acid, ammonia and tar and tar derivatives may be recovered as by-products. The charcoal thus obtained is equal to first rate wood charcoal for metallurgical work. There are well established peat coke plants in Europe, which have been running a number of years.

The most promising use of peat is in gas producers for generating power or fuel gas. Plants equipped with properly designed gas producers, with or without apparatus for the recovery of by-products and located near the bogs from which the fuel is taken, are being successfully operated in a number of European countries to generate electricity for lighting and power purposes in nearby towns. Some of these plants use peat with as high as 60 per cent moisture and are reported to recover enough ammonia as the sulphate to pay the cost of getting the fuel and running the plant.

The fuel value of perfectly dry peat ranges from about 7,000 to above 11,000 B. t. u. This is reduced by the presence of moisture, high ash content.

It would seem that our peat resources are well worth developing whenever additional fuel supplies are needed for the development of the country.

SOME ECONOMIC ASPECTS OF CONSERVATION

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CONTENTS

INTRODUCTION

PAGE

- 1 Conservation defined
- 2 Conservation and industrial evolution

PART I

Conservation and Individualism

- 3 *Laissez faire* the major premise of American democracy
- 4 Conservation may be in conflict with self-interest
- 5 Conservation and the rate of interest
- 6 Conservation must compete with business opportunity
- 7 Current contingencies may forbid conservation
- 7 Conservation implies inflexible investment plans
- 8 Similarity of methods of reclamation and conservation
- 9 Latent resources constitute poor credit security
- 10 Costs of conservation
- 11 Life-interests of individuals imply progressive costs
- 12 Conservation finance
- 12a Conservation accruals illustrated
- 12b Diagram illustrating conservation accruals and costs
- 12c Table of accruals and costs of initial conserve of \$100
- 13 Conservation implies higher prices
- 13 Monopolies and conservation
- 14 Conclusions

PART II

Conservation and Collectivism

- 17 The nature of collective interests
- 18 A public defined
- 18 The nature of public property
- 19 Differential public property in natural resources
- 20 Public saving may neglect the rate of interest
- 21 Conservation on the public domain
- 21 Credit facilities for public conservation
- 22 Conclusions

Few terms are so much used and so little defined as *conservation*. The circumstances attending and following the introduction of the "conservation idea" in the United States have given the word a popular appeal which is not altogether fortunate. Five years ago, *conservation* was made to convey to the public consciousness a more or less vague and idealistic politico-economic policy which seemed to promise an enlarged general welfare in the future at no considerable personal expense or present sacrifice. The word soon became the handy shibboleth of divers propagandists and dissembling publicists, and today *conservation* stands for no concrete doctrine or policy, the word itself having been stripped of entomological descriptive or denominative value.

CONSERVATION DEFINED

I shall not make issue with those who, perceiving that *conservation* was in the way of becoming a catch-phrase signifying beneficent economic policy, garbed the term in an overclothing of sociological, biological and political rayment in their endeavor to popularize doctrines and projects which are in no way concerned with the management and utilization of the natural resources of the earth. *Conservation*, as herein used, pertains only to the fostering of natural resources of economic production, and signifies methods of social thrift designed to contribute to the perpetuation and judicious utilization of natural materials and instrumentalities. *Conservation is, therefore, defined as a dynamic economic policy directing a providential administration of the natural agents of production and enforcing prudential restraint in the consumption of the physical resources of the earth.*

The above definition is obviously elastic. "Providential" and "prudential" are words of variable and possibly of conflicting attributes when used to severally characterize individual, community, national and cosmopolitan interests. "Consumption" may imply rational exhaustive use, wasteful misuse or nonuse, deliberate destruction of utilities, or it may imply a perpetual and non-exhaustive usufruct of natural agencies. "Restraint" conveys a meaning more or less abstract and relative because of various conceivable conditions and degrees which might be satis-

fied by the voluntary exercise of individual reasoning and self-will or of public opinion, or might require the suppressive action of a vigorous police power along several lines of administrative regulation. However, the definition is so drawn that *conservation* assumes a definite and unmistakable meaning under given economic conditions and specific social ideals.

CONSERVATION AND INDUSTRIAL EVOLUTION

In arriving at the significance of conservation and the significant attributes of a conservation policy, it is quite necessary that account shall be taken of the stage of industrial evolution and that distinction shall be drawn between the respective logical concomitants of socio-economic motives of individualism, of sectionalism, of nationalism, and of cosmopolitanism. I may add here, in anticipation of subsequent analysis, that "conservation" is not necessarily antithetic to "exploitation"; indeed, exploitation, development and conservation of natural resources are logically consistent and correlated, and, properly interpreted, they signify respectively successive stages in the process of rational appropriation of physical utilities to social needs.

I

CONSERVATION AND INDIVIDUALISM

An individualistic economy arises from the general acceptance of the essential elements of the *laissez faire laissez passer* doctrines of popular sovereignty and passive government. *Individualism* predicates certain "natural rights" and characterizes economic and political institutions by admitting a preeminence of individual rights and privileges over non-personal collective interests. Exclusive proprietorship, arbitrary bequest, unrestrained contract, and universal opportunity to acquire wealth by productive processes, by appropriation and by bargaining, are thereby declared to be "inalienable" private rights. Such rights constitute "freedom," and individual liberty is accepted as the criterion of human well-being. Government assumes a menial role, being

confined in its functions to the protection of individuals in the pursuit of wealth, in the utilization and maintenance of property, and in the exercise of liberty.

Laissez Faire the Major Premise of American Democracy

The presumption of personal liberty and passive government, obviously illogical in its bold statement and fictitious as a doctrine of universal or permanent freedom, constituted the original hypothesis of American democracy, and, slightly impaired, it stands to-day the major premise of our popular economic thought and our business activities.

The passing of *laissez faire* is about accomplished in the foremost nations of Europe. Doubtless, there have been periods in the evolution of nations when the ascendancy of individual initiative in the pursuit of private rights and consequent exclusive privileges made for relative economic efficiency and social progress. This was probably true during and immediately following the industrial revolution in England; it was true during the pioneer period of American development. Recently, surface changes have taken place which indicate a reaction against *laissez faire* in our social and political organism; but, as yet, industrial and commercial institutions in the United States remain substantially subservient to the economic philosophy of the eighteenth century.

Conservation may be in conflict with self-interest

I do not contend that conscious self-interest obtains in our economic thought and action to the exclusion of collective interests and altruistic motives; but there does exist a strongly entrenched utilitarian individualism which will stubbornly resist any attempt to subordinate private rights to general welfare, to place social production above personal acquisition, to jeopardize private riches in the promotion of national capacity, or to reserve available utilities in contemplation of the probable needs of an indefinite future. If conservation is to be carried farther than the mere statement of an academic doctrine of general

beneficence, the conservationist must formulate a dynamic program, and, in justice to his own intellect, he must exemplify the economic theory upon which he proceeds and explain the bearing of a conservation program upon existing institutions and the consequent lines of divergence from prevailing economic practices.

Conservation and the rate of interest

When coordinated with the individualistic conception of property and property-use, conservation is normally confined to a policy of deferring the enjoyment of privately owned natural utilities until such times as shall be consistent with the realization of a maximum of satisfaction by the respective proprietors. If such satisfaction be expressed in terms of *value*, conservation policy is nothing else than pecuniary acumen and good business organization. The process involves temporary abstinence, possible outlays, and a period of waiting, which can be justified in the minds of proprietors by no other consideration than that of an enlarged enjoyment in realization subsequent to the period of restraint. In any conceivable case, the period of restraint must be a time of augmenting values, and under most favorable conditions the conservation period can not be extended beyond such time as will permit the proprietor to realize maximum net returns in the utilization of his resources.

It must here be emphasized that, individually considered, use and enjoyment in their relation to utilities are not always, indeed, not usually, identical with *value*; and accruing value-increments may not be taken as reliable criteria of change in subjective worth. However, for the sake of analysis, the abstinence, expense or deprivation involved must be conceived of as financially analogous to the process of saving and investing in contemplation of a future return which shall incorporate a value-increment of *conservation-growth* by way of interest.

Conservation must compete with business opportunity

To the business mind, conservation, if it is to become an effective motive, must mean something more than the hoarding

of available values against future needs; it must afford an investment proposition sufficiently attractive to command the voluntary acquiescence of proprietors in the sacrifice of actual or imminent income and alternative investment opportunity in anticipation of profitable return in future values. Such a proposition must combine the conventional requisites of a substantial investment; namely, (1) an increase in value which shall constitute a rate of interest and profit sufficient to justify the personal sacrifice of the proprietor, and (2) a final maturity and an interest or dividend period which shall suit his convenience or necessity.

It now becomes clear that the measure of increased values of conserved resources, taken in its relation to prevailing interest rates and business profits, is a necessary test of expedient conservation when privately owned resources are concerned and when private property is politically immune from the burden of a public interest and from official management.¹

Current contingencies may forbid conservation

The formula of *ideal interest* is not the final test of the feasibility of conservation of privately owned resources. As above implied, there are those who are not in a pecuniary position which makes it personally agreeable to exchange goods in hand for future goods at any premium, unless, indeed, the premium be made immediately available in present purchasing power by way of "discount" on future values. Others are so psychologically constituted as to be more or less blind to *prospects* when in the presence of *opportunity*. There are others who, because of their attenuated expectancy of life, prefer to make no concessions to the future. Consequently, conservation reduced to the basis of investment at prevailing rates of interest or at any commensurate rate would seem to command the concurrence of relatively few proprietors.

¹ From the above reasoning, there appears tentative cause for considering natural resources which are subject to conservation management as removed from the operation of the economic laws of *rent* and made subject to the laws of *capital* and *interest*.

Conservation implies inflexible investment plans

A second obstacle to the operation of conservation on the basis of interest costs appears in the fact that to the business mind a desirable investment plan must supplement an adequate rate of interest with a definite maturity and a satisfactory realization; that is to say, the "time-form" of the investment is important.¹ Private investors seldom desire a maturity beyond their own expectancy of life or that of their immediate dependants; some prefer to receive their investment proceeds in a lump sum at a specified time, others must needs provide for annuities, others may undertake only such investments as can be liquidated at will.

It is unnecessary to detail the essential attributes of private property which will admit of restrained or deferred utilization of productive agents only upon one or other of the above specifications. If a freeholder is not to be deprived of his traditional and constitutional rights, he may and will impose such conditions as are to him the necessary or convenient alternatives of arbitrary use, whatever may be the sacrifice of future social values or the injury to possible future well-being. *Any conservation scheme which tends to restrict an owner's arbitrary use or disposition of natural utilities held in private title is futile which does not circumvent the anomaly of inviting proprietors to undertake virtual investments which they can not, in consideration of pecuniary circumstances, afford, and which do not incorporate the essential investment attributes of certainty, flexibility and convenience.*

Similarity of methods of reclamation and conservation finance

The investment aspects of conservation suggest the identity of the financial problems here involved with those associated with development and reclamation. In either case, the proprietor must assume the role of capitalist, or he must hypothecate his holdings and fund his project by soliciting credit. In the latter instance, which is the usual one, the investment seeks the

¹ Fisher; *The Rate of Interest*, Chap. VI.

open money market, and conservation projects, as have reclamation projects, will be forced to compete with current commercial and industrial activities for financial support.

Latent resources constitute poor credit security

The owner of *convertible commercial assets* always commands credit which enables him to borrow at his convenience to a considerable proportion of the present worth of his securities. In this way, during delayed commercial processes, he may hasten or level his income-flow by discounting at bank a portion of his anticipated revenue to present worth and immediate realization. Likewise, the industrial promoter and the reclamationist logically calculate the necessary lapse of time pending the maturity of an undertaking and the probable annual revenues and commercial values to follow, and, upon the pledge of such definitely timed and estimated future values, funds may usually be had by the hypothecation of mortgages and the issue of bonds. If, however, one be the proprietor of reserved natural resources subject to a restricted rate of utilization or to direct appropriation only after the lapse of an indefinite period of time, his proprietorship interests are not "convertible," they may change in value at an uncertain and irregular rate, and the futurity of realization is indeterminate; consequently, the owner occupies an unfavorable position as regards borrowing power, despite the fact that his resources may be of great potential worth.

Latent productive agents, particularly unimproved lands and other undeveloped natural resources, are universally regarded as relatively poor credit security, and indeterminate periods of credit extension are designated as "speculative" and are avoided by most funding institutions. Doubtless, short-time conservation projects on private estates may be successfully financed, even when credit is necessary to enable the proprietor to defer utilization. Credit periods, however, must be confined to approximate maturities which shall be adjustable to conventional funding arrangements and limited in time to the temporal expectancy of the proprietor. The absence of either of these conditions eliminates the possibility of promoting conservation

by means of private credit and, in fact, destroys the interest of owners in conservation projects involving their own property. Identical obstacles have forced individual enterprise and private capital from the field of reclamation development and the intervention of public credit and government initiative has become imperative—not only in the United States, but wherever arid lands are being subjected to irrigation. In this situation the contradistinction between certain characteristic attributes of private and public economics is spontaneously revealed.

Costs of conservation

The problems of conservation are concerned with present deference to the future. Individually considered, this invariably necessitates a sacrifice of immediate income or accumulation to be compensated for in the future. Compound interest, or an equivalent discount, is the minimum price which must be paid in this exchange between present and future goods. From the standpoint of the owner, conservation, either at the cost of deferred use and restricted marketing, or by less wasteful and temporarily more expensive production, is in conflict with the economic law of *technical superiority of present over future goods*. It threatens to ignore that personal interest which Professor Fisher calls "time preference,"¹ which John Rae called "effective desire for accumulation,"² and which Bohm Bawerk designates as "perspective undervaluation of the future."³

This very effective bias toward value in hand is the sole justification of interest charges, it is the basis of generally accepted interest theories; it emerges from five human attributes which are of the nature of *personal disabilities*; namely, (1) unsatisfied present wants, (2) lack of foresight, (3) lack of self-control, (4) limited expectation of life, (5) attenuated or transitory interest of individuals in society.

¹ *The Rate of Interest*, p. 88.

² *Sociological Theory of Capital*, p. 54.

³ *Positive Theory of Capital*, Bk. V, Ch. III.

Life-interests of individuals imply progressive costs

What the periodical or total increment must be to compensate possible conservation costs to individuals, extends beyond the sphere of ideal interest and discount and admits the additional consideration of the transitory interest of a single life in temporal affairs. Theoretically, it appears that the minimum value-increment must be identical in amount with the proceeds of prevailing interest rates subject to continuous compounding for a period commensurate with the proprietor's normal expectancy of life or the probable futurity of his social interests. If the proceeds of conservation are to be withheld beyond the life-interests of present owners, no value-increment, however great, will command the consideration of proprietors when placed in subjective contrast with the delights of present or imminent realization. Nor does the introduction of corporate ownership—a proprietorship of indefinite succession—modify this principle, for stockholders have adequately demonstrated a tendency to arbitrarily exercise immediate self-interest through the agency afforded by the private corporation. Consequently, no scheme of conservation is admissible under the tenets of individualism and private ownership unless—(1) anticipated values are discountable to present worth and the proceeds made available at the will of the owner, or (2) conservation increments are periodically realizable after the manner of annuities. The first proposition is analogous to purchase at approximate market price. The second plan involves the operation of a rate of conservation-growth which would advance in value from the *minimum* above indicated to *infinity*, the rate being concurrently commensurate with the reciprocal of the proprietor's constantly diminishing life-interest.

Conservation accruals illustrated

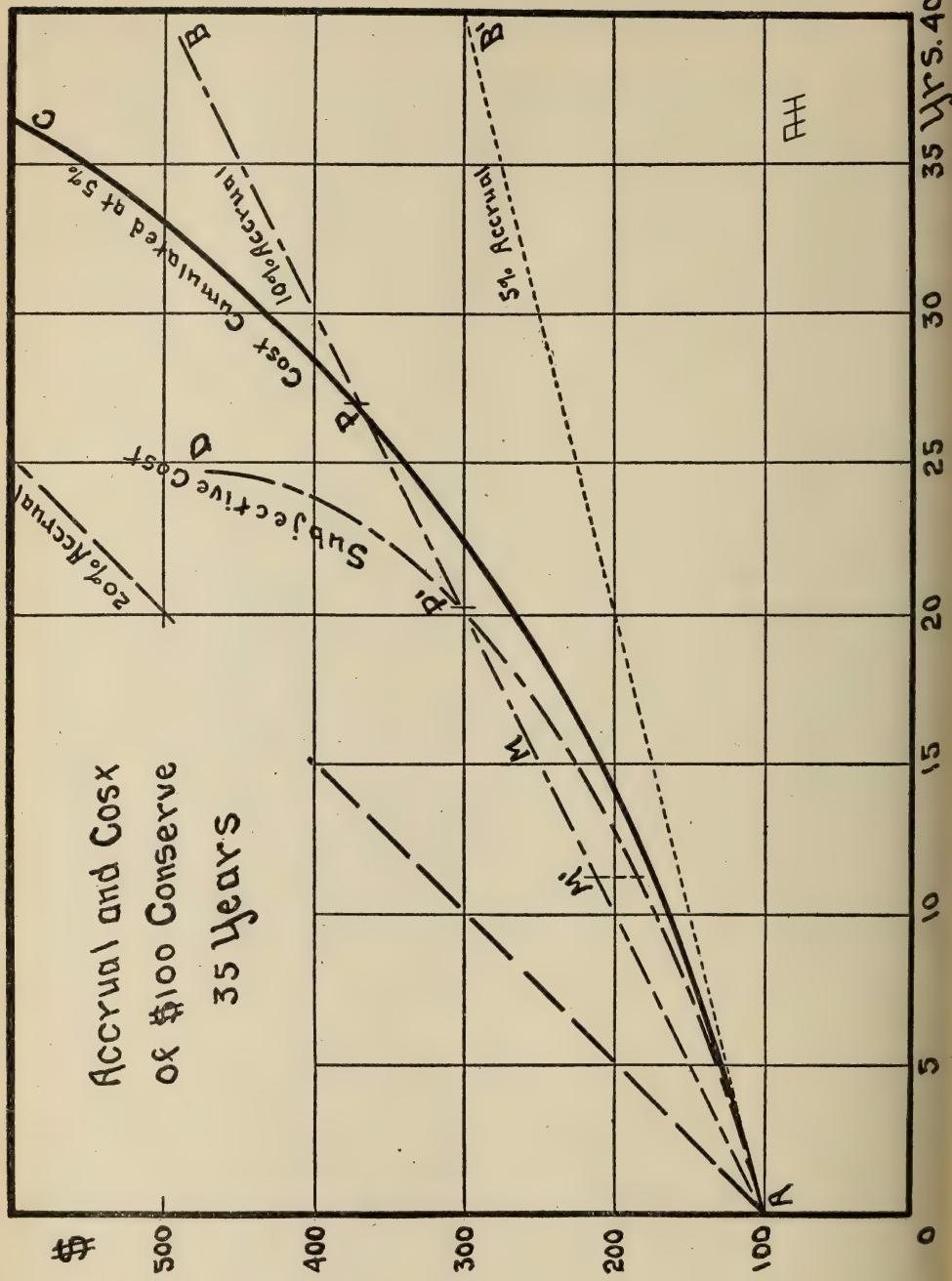
Figure I assumes that an available income of \$100 is deferred in the promotion of a conservation enterprise. It is also assumed that the \$100 *conserve*, permitted to remain intact incorporated in the natural resource, may *grow* at an annual rate of 10 per cent. for an indefinite period, as indicated by the length and pitch of

the line AB. If funds are worth 5 per cent., the actual carrying expense of the project would involve a 5% interest rate cumulatively compounded to successive amounts indicated by the line AC, and the undertaking would afford a profit to the proprietor indicated by the relation of the line AB to the line AC. There would be an annual surplus of conservation growth over carrying expenses for about 15 years (M), at which time the \$100 would have grown to \$250 at a maintenance cost of \$107.89, accounting a net profit of \$42.11 after which the net surplus would decline for 12 years (P). Thereafter, carrying charges would annually exceed conservation-growth resulting in a cumulating loss sufficient to extinguish antecedent conservation accruals by the middle of the twenty-seventh year.

Now, if conservation proprietors involved have an average expectancy of life of 25 years and no pecuniary interest in survivors, this personal subjective factor will not be reflected in the market rate of interest and they will normally discount the expected proceeds of conservation at a rate which tends to progress even more rapidly than compound interest, say proportionate to the pitch of the line AD. In this case, the maximum *effective* conservation surplus would be reached at a somewhat earlier date (M'), and after about the twelfth year the project would probably be abandoned.

Lesser increments of conservation-growth would afford correspondingly lower profits and shorter terms. A 5% accrual, represented by the line AB' would involve a loss to the proprietor from the start. Conversely, higher rates of annual accrual would extend the period and the amount of net surplus.

Accrual and Cost
of \$100 Conserves
35 Years



Successive conservation accruals of \$100 subject to respective annual increments of 10% and 20%, funds being worth 5%. (No outlays contemplated.)

| Years | Value Increment | | Cost of Conservation | Net Increment | | Average Annual net Increment | |
|-------|-----------------|--------|----------------------|---------------|---------|------------------------------|---------|
| | | | A | B | A | B | A |
| | A(10%) | B(20%) | | | * | * | |
| 1 | \$110 | \$120 | \$105.00 | \$5.00 | \$15.00 | \$5.00 | \$15.00 |
| 5 | 150 | 200 | 127.62 | 22.38 | 72.38 | 4.48 | 14.49 |
| 10 | 200 | 300 | 162.89 | 37.11 | 137.11 | 3.71 | 13.71 |
| 15 | 250 | 400 | 207.89 | 42.11 | 192.11 | 2.74 | 12.81 |
| 20 | 300 | 500 | 265.33 | 34.67 | 234.67 | 2.23 | 11.73 |
| 25 | 350 | 600 | 338.64 | 11.36 | 261.36 | .45 | 10.45 |
| 30 | 400 | 700 | 432.19 | -32.19 | 267.81 | -1.07 | 8.93 |
| 35 | 450 | 800 | 551.60 | -151.60 | 198.40 | -5.33 | 5.96 |

From the diagram and table it appears that, if funds are worth five per cent. and no outlays are required, conservation projects contemplating an average annual premium of ten per cent. on deferred utilization may logically be undertaken on a twelve-to fifteen-year futurity, variation being due to the subjective influence of particular life-interests involved. The net conservation-increment at the end of the fifteenth year would amount to 42.11 per cent. of the initial *conserve*. If a twenty-per cent. premium on conserves is anticipated, the maximum conservation increment would not be reached until the thirtieth year, at which time the net increment would reach 267.81 per cent., being an average annual saving of \$8.93 over and above the principal with interest at five per cent. compounded annually, amounting to a gross accrual of \$700 on a conserve of \$100.

Conservation finance

The only possible means of circumventing the apparently prohibitory financial obstacles to the successful conservation of privately owned resources of production is the creation of a credit system which shall recognize and calculate the possible excess of future over present values incident to the utilization of such resources and the probable rate of value accrual; and

which shall afford the private proprietor the alternatives of *arbitrary utilization or compensatory values* payable in advance or by means of direct or indirect annuities.

If land banks were widely established and adequately capitalized they might operate, as they have in other countries, to mitigate the physical waste of soils by neglect, over-cropping and under-fertilization. If forest risks were sufficiently reduced as a preliminary conservation measure, some plan of mortgage security and bond issue might be devised for carrying the conservation expenses of certain forests. Such measures have passed the experimental stage, but they promise slight aid in solving the larger problems of conservation finance. The fact remains that proprietors of mines of unknown content, owners of forests subject to fire loss and uncertain annual taxation, and possessors of water-rights of indefinite future value, are practically without bankable securities when in need of funds and each must bait current opportunities and early markets. In such cases, conservation and private property are incompatible. In any case, a policy of conservation can not disregard what economists call "percentage excess of present desirability"; and this condition burdens conservation with an interest charge or a realizable discount which proprietors are certain to demand and which must be paid from the public purse in consideration of resulting *general welfare* or be shifted by a system of bonded indebtedness upon the beneficiaries of the future in consideration of *value to be received*.

Conservation implies higher prices

Since the inauguration of effective conservation tends to reduce market supplies, it is obvious that there would appear a resultant tendency to higher prices. Furthermore, since the burden of current production would temporarily fall more heavily upon labor and capital, a tendency to decreased returns upon these factors of production would be logically expected.

Monopolies and conservation

It is an established practice of natural monopolies to restrict the rate of utilization of monopolized resources. This is held by the friends of some such organizations to be an effective and rational means of conservation. It is difficult for economists to follow a line of reasoning which will lead to this conclusion. Monopoly power affords a means of circumventing the financial obstacles to the conservation of privately owned resources by avoiding competitive valuation of products and securing the equivalent of "realizable discount on future value-increments" in monopoly prices exacted from the present consumer with a strong probability of a similar excess exaction from future consumers as well. This is not conservation. It is *reservation* of certain resources as a means of exacting "earnings" in excess of costs of production. This excess tends to approximate double the cost of legitimate conservation, and may stimulate the consumption of substitute utilities, thus defeating any net social saving for future needs.

In so far as the costs of conservation may be charged to consumers in advanced prices and the burden of production temporarily shifted from the land so as to rest more heavily upon labor, the *actual cost of living* will be advanced. The manner in which these tendencies may be controlled is necessarily deferred as a part of the treatment of public economics in relation to conservation.

Conclusions

Concerning the feasibility of the conservation of natural resources which have passed into private proprietorship, one is forced to the conclusion that the effective limits of any plan are so restrictive as to permit little progress except in the promotion of soil conservation. To be made practicable, a general policy for the promotion of conservation upon private estates must contemplate methods of reducing the intensity of *effective desire for accumulation* among owners or of so diverting its influence as to admit of a more economic utilization of certain resources. The following methods are applicable:

(1) *The organization of credit facilities which may advance to proprietors an amount which shall approximate the discounted values of conservation-growth upon the hypothecation of conserved properties, thus parrying the assault of present pecuniary interests upon natural resources which should be conserved.*

(2) *The publicity of such expert advice and demonstration among private owners as will lead them to recognize the value advantages of a definite plan of rational utilization even though it involve temporary retrenchment, thus enlisting their efforts toward conservation upon the motive of actual personal gain.*

(3) *The direction of educational ideals along such lines as will tend to alleviate those personal disabilities which give rise to overkeen self-interest in present values (See p. 11) by the development of such compensating qualities of character as contentment, foresight, self-control, altruism and interest in the public good.*

That the significance of the above assumptions and conclusions may not be mistaken, it is reiterated that purely individualistic motives in the exercise of proprietorship interests are assumed. Such motives, however, are always tempered with a measure of altruism which is rarely altogether personal. This being true, the apparently prohibitive economic barriers of individual interest must admit of some personal concession to the general good and to future welfare. "Genuine private affections, and a sincere interest in the public good, are possible, though in unequal degrees, to every rightly brought up human being" (John Stuart Mill; *Utilitarianism*, p. 21).

II

CONSERVATION AND COLLECTIVISM

In passing from the contemplation of conservation under the operation of private property interests to a discussion of certain public interests in natural resources, I shall make four predictions which justify a fundamental distinction between the attributes and objectives of an individualistic and a collective economy.

(1) Economic arrangements which afford opportunity for the

attainment of maximum pecuniary advantages of individuals are not always contributory to or consistent with a high level of general or group well-being.

(2) Effective economic interests of certain lineal social groups may differ or diverge from the determinant interests of one or a few generations of individuals within the group.

(3) Collective interests may at times fall in conflict with individual interests; in such cases, personal preferences may be subordinated to public necessity and convenience.

(4) The passive attributes of *laissez faire* government are inadequate to define and administer collective economic interests, consequently, additional government functions and agencies become necessary to the promotion of the general welfare.

The nature of collective interests

Two important economic hypotheses emerge from the recognition of a *public welfare* which may command preference over *individual well-being*. (1) Physical sources of production may be so burdened with a collective interest as to become plausible objects of public property. (2) Property interests of a collective nature are coordinate and coextensive with the joint motive of the group in which they are vested, and are therefore immune from certain "disabilities" of freehold property which arise from the motivation of the "technical superiority" of present personal utilities.

A Public defined

The *public* from which spring the motives of a collective interest may be nominally identified with a national state, a group of states, or a civic division of a state. Again the delineation of a public may appear to rest upon geographic rather than civic characteristics, or may fall within certain stratifications of society which chiefly distinguish economic classes. *For the purpose of this treatment, any considerable group of individuals, having more or less definite and permanent collective economic interests which are independent of and possibly inconsistent with concurrent individual interests, is a public.* Such collective eco-

nomic interests, in so far as they are associated with the material factors of production, constitute the economic justification of public property.

The nature of public property

Property rights and powers may be active or latent, they may be actual or contingent, they may be vested severally, jointly, or in differential proprietorship. By differential proprietorship is here meant the legal separation of associated property attributes and their respective lodgment with different proprietors. Differential proprietors are mutually obligated with respect to the property object; thus, one person may be entitled to the possession and use of a property-object subject to the contingent power of another to assume possession or to regulate the use under given conditions or eventualities, at specified times and for certain purposes.

Differential public property in natural resources

Property in natural resources incorporates certain differential rights and powers respectively coincident with possession, utilization and control. The public interest in a natural resource may be exclusive or partial, and may change in its qualitative relation to coexisting private interests in accordance with social and economic conditions. The recognition of differential proprietorship is destined to become significant in the development of conservation. A distinct public interest arises from the actual or potential collective dependence of the people of a state, of a district or of an economic class upon the capacity of available productive resources and coordinated distributive agencies which contribute to their common welfare. The necessity of differential public property has long been recognized in the arid districts of western America, where the *usufruct* of irrigation waters is a private right, but private proprietors are subordinated to the State in its exercise of power over the moment of the use consequent to the *public ownership of the stream*.¹ The general prin-

¹ Constitution of Colorado, Art. 16, par. 5.

ciple here involved is clearly set forth in the well known dictum of Chief Justice Hale—"when private property is affected with a public interest it ceases to be *juris privati* only."¹

The recognition of collective interests and of public property in any form, modifies the theoretical economic considerations advanced on a previous page as pertaining to a regime of exclusive private proprietorship and individual interests. With the possible ascendancy of public interests over private interests in the utilization of certain productive agents, the dominance of the public differential in property is justified and the power of government control should consequently be defined and functionalized.

Public saving may neglect the interest rate

The conservation of natural resources held in public property, as is true in the sphere of private property, is a process of saving or investing, or both. The measure of savings in any instance being a cumulation of initially deferred income, the outlays necessary to carry the project, and the spontaneously accrued values awaiting utilization. But this reservation and accumulation of utilities has no significance as a provision against the eventualities of declining years of individual lives or in behalf of continuing personal interests in society; in fact, public properties as such are essentially subject to no individual interests and respond to no economic laws based upon the subjective springs of individualistic motives. Because of the relative perpetuity of public interests and the insignificance of years in the life of a society, the "*superiority of present goods over future goods*" and the consequent annual interest charge or rate of discount which obtains in the sphere of private economics, have little theoretical significance and in the practice of conservation may become quite negligible.

Conservation on the public domain

If the above reasoning is accurate, conservation upon the *public domain* is not hampered by the consideration of accumulating interest charges against deferred utilization, nor is there

¹ *Munn vs. Illinois*; 94 U. S. 113.

necessity for justification of conservation policies in physical growth or even price increment. Conservation may here assume the nature of hoarding; social thrift may legitimately disregard certain market demands for exhaustible natural utilities at prices which would yield large profits above the current cost of production—prices which would immediately appeal to the private proprietor, but which might not properly account that part of the *social cost* of production which may be shifted upon the future. If, however, any actual outlay be incurred in protecting or developing the property during the period of conservation, the amount with interest should be made available as a discount upon the future and charged to the proceeds of the project.

Credit facilities for public conservation

The question of credit, as a necessary concomitant of conservation, reappears at this point. But here the problem of finance is much simpler than that presented by the possible necessity of discounted total future values to compensate individual proprietors for deferred or restrained use. The expenses of conserving publicly owned resources may be easily and legitimately provided by the issue of guaranteed-interest mortgage bonds against the property; the funding of interest and maturities being so arranged as to rest the costs equitably upon the beneficiaries of the project for a period extending if necessary into generations. Furthermore, public credit, supported by the tangible values of conserved properties and the taxing power of the government, is more readily and cheaply funded than is any form of personal credit bearing like futurity.

Conclusions

In view of the characteristic freedom of public property from the operation of certain *priority claims* and *arbitrary powers* which obtain in the sphere of private property, the following postulates appear.

(1) *The conservation of such public property as is not inseparably associated with an effective private interest may be economically*

justified as a saving of utilities now available until a time of more intensive need, regardless alike of the interval to elapse before utilization and of the amount of the possible annual value-increment consequent to deferred consumption.

(2) *Although some value-increment is the logical expectation of successful conservation, the theory of interest has no part in explaining the raison d'etre of conservation or in measuring the probable or necessary value-result of a conservation project or policy, in so far as it pertains to public property and collective interests.*

(3) *Actual outlays necessary to maintain conserved resources in status quo, or to promote preliminary development, should be within the amount of the anticipated value-increment, and should be currently compensated by bonding future proceeds of the project to the amount of such maintenance costs with interest.*

Time does not here permit the development of a closer approximation to the circumstantial limitations which economic theory places upon *conservation*. Enough has been said to demonstrate the necessary correlation of the principles of conservation and conservation policies with certain socio-economic institutions, chief among which is *property*. The descriptive correlations above established may obtain only as between conservation and dissociated private property in the one instance, and between conservation and dissociated public property in the other. That comparatively few natural resources will permanently fall entirely within either one or the other of these contradistinctive designations is improbable; indeed, the chief concern of the "conservationist" to-day, and of the "landed opportunist" as well, is directed toward natural resources which typify physically associated attributes which may be economically differentiated as between public and private interests. Furthermore, the dominant private interests of yesterday are being overtopped by the public interests of tomorrow; and the opposite transformation, while less common in this country than in times past, is by no means obsolete.

The respective factorial significance of individual interests or of collective interests, of private property-rights or of public property-powers, is in most cases one of proportion—there are properties of a primarily private nature which are affected with a

public interest, and there are properties of a public nature affected with a private interest. In any given case, the conservation project must be so designed as to comprehend the role of each property factor actually or potentially concerned, and must be predicted upon a combination formula derived from the postulates above described with due deference to respective interests concerned.

THE NATIONAL PHASES OF THE MINING INDUSTRY

J. A. HOLMES,
Washington, D. C.

The American ideal is a great nation composed of great states, and each state made up of the largest possible number of well-to-do communities and individuals, or families, all transacting business or seeking pleasure with the minimum of statutory or governmental interference consistent with the public welfare. This was the fine ideal established by our forefathers. With the increasing density of our population and the increasing complexity of our modern commercial and social fabric, it is becoming less and less easy of realization.

In many respects the welfare of the individual, the welfare of the State, and the welfare of the Nation coincide; but they do not always, in all respects. Generations come and go; the life of the individual is short; his plans and ambitions relate to temporary purposes and present profits. The State and the Nation go on forever; and the State and the Nation must therefore safeguard their own future.

The individual sometimes becomes strong by trampling under foot or ignoring the rights of others; he has often become rich through profiting unduly from the labor of his associates, or through a wasteful and destructive use of resources which he neither created nor increased in value, and which are essential to the permanent welfare of the community. The state and the nation must protect the weak, and must promote the welfare of all their communities and all their citizens.

Thus far, the American State has considered primarily and mainly the opening up and development of its resources. With this end in view it has employed its geologists and its engineers and its chemists. Each state has explored and advertised its resources, and has invited both domestic and outside capital to participate in their development.

In their anxiety for growth and development, the states have

in some cases failed to enact or enforce legislation necessary to properly safeguard the lives of miners; and with a few exceptions, and these coming almost too late to be effective, none of the states has enacted and enforced legislation looking to the prevention of waste in the mining and utilization of its mineral resources. The enactment of effective legislation along either of these lines has been often hindered by the general fear that such legislation would work to the state's temporary disadvantage in its developmental rivalry with other commonwealths. In some cases the states have shown, what is in some respects, a commendable desire to reserve for the exclusive use of their own citizens such natural resources as happen to be located within their own political boundaries.

Meanwhile, the National Government, through the general welfare and interstate commerce clause of its Constitution, has endeavored to safeguard the welfare of the nation as representing the welfare of all the states, by requiring that the resources located within the political boundaries of any state, when available for use shall be available for use as a basis for industries in all the states; and it further arranges for such exchange of resources and manufactured commodities between this and other countries as may be requisite and available for our continued national development and growth.

In considering the possible activities of the individual and the State and Federal Governments in behalf of a more rational use of our mineral resources, certain facts and principles should be kept clearly in mind: namely,

That the present generation has the power, and it will exercise the right to use so much of its resources as it actually needs; (no such thing as bottling up resources).

That the Nation's needs are not likely to be curtailed; these needs will increase with the extent and diversity of its industries, and more rapidly than its population increases; and

That the men of this generation will not mine, extract, or use these resources in such manner as to entail continuous financial loss to themselves, in order that something may be left for the use of future generations.

Furthermore, it should be understood that the mineral resources

of the country have required long ages for their accumulation; that of these resources the nation has but the one supply; and when that supply has been exhausted there are no known substitutes available for use in meeting the nation's further needs; and that, to the best of our present knowledge, this one supply must therefore serve as a basis for both the present and future needs, the future needs to be far greater than those of the present day.

The following facts illustrate the growing demand upon our one supply of mineral resources:

The per capita consumption of coal in 1870 was less than one ton; in 1890, two and one-half tons; and in 1910, it was five and one-half tons.

The per capita consumption of iron in 1880 was 200 pounds; in 1910 it was 665 pounds.

In 1880 the per capita consumption of steel was 55 pounds; while in 1910 it was 634 pounds.

In 1890 the per capita consumption of cement was 70 pounds; in 1910 it was 317 pounds.

In the highest sense, (therefore) our mineral resources should be regarded as property *held in trust*, for both present and future needs of the nation; for it should be remembered that no human labor or other human agency has contributed to their origin or their intrinsic value; and that whatever rights the individual may possess have been derived from the State, the original owner. The State does not surrender its right, nor should it neglect its duty to safeguard the welfare of its future citizens by preventing the wasteful use of these resources. While the individual may, therefore, claim the right to use the resources in proportion to his needs and the actual needs of the community, he certainly has no right to waste that which is not now needed for present use, and which is certain to be needed hereafter.

In our rush for present day prosperity let us not forget that measured in the terms of the needs of this great and rapidly growing country, our resources are *limited in quantity* and we have for the needs of all time *but this one supply*; and

Measured in the terms of the life of the nation, at the present increasing rates of consumption and waste, we will, while the

nation is yet in its infancy, exhaust the resources necessary for its future welfare.

Therefore, the right of the present generation to the efficient use of these resources carries with it a sacred obligation not to waste this precious heritage.

The proposition that we need not worry about using up our resources for the reason that when these are gone some now unknown substitutes will be found to meet the needs of future generations is even less sound than the proposition to a farmer that he need not use carefully his newly harvested crop, because if he uses it up long before the end of the year, his needs will be cared for in some mysterious way.

No other country is so amply provided by nature with resources that make for national greatness; no other country has, therefore, within its own territory, so large a measure of these resources which, if wisely used, will serve as a basis of continuous growth and permanent national welfare.

Furthermore, in considering our fuel supplies, it may be well for us to remember that both Canada on our north, and the American republics to the south of us, are, in comparison, poorly supplied with coal; and therefore, if the United States, through a more efficient mining and use of its coal, has a larger supply than it requires at home, it may wisely export its surplus to these countries in exchange for other raw materials needed in the maintenance of its own varied manufacturing industries.

As illustrating the need of reform in behalf of greater safety and greater efficiency in the mining industries of the United States, attention may be called to the fact that during the past ten years more than 30,000 men have been killed, and more than 60,000 men have been injured in our mining and quarrying operations. And nothing could better illustrate our wasteful methods than the fact that during the past year in our coal mining operations we left underground, in such condition as to make it practically unrecoverable in the future, more than 250,000,000 tons of coal. Of natural gas we lost forever, during the past year, by turning it into the atmosphere, a supply greater than the aggregate quantity of the artificial gas manufactured in all the cities and towns of the United States.

Wastes in some other branches of the mining and metallurgical industries of the country are less extensive and perhaps less easily remedied. The progress made through the efforts of individual mining and metallurgical engineers has been large and commendable; but at almost every turn there is serious waste, and, therefore, need of further improvement.

At your Founders' Day exercises, October 7, 1911, President McRae of the Pennsylvania Railroad Company, in an address full of thought and inspiration, called attention to the fact that where a state has its resources already well developed "then comes the time for a most careful conservation of what remains."

This wise advice applies with special force to the State of Pennsylvania. Having within its territory almost the only supply of anthracite coal known in the country, which supply occupies an area of less than five hundred square miles, and which at the present rate of consumption and waste can hardly be expected to last much beyond a hundred years, with a supply of bituminous coal estimated to be less than that in either Illinois, Colorado, Utah, New Mexico, Wyoming or West Virginia, it produced in the year 1910 25 million tons of coal more than the production of all of these states combined. It has in its south-west counties admittedly the largest and finest bodies of coking coal to be found in the country, and yet it is using these coals at so rapid a rate and in so wasteful a manner that the present supply will almost certainly be exhausted in less than fifty years. Practically all of this coal is being coked by the old wasteful bee-hive methods and possible by-products to the value of probably thirty million dollars per annum are being turned loose into the atmosphere.

A few years ago the inhabitants of Pittsburgh might see at almost any time from a single viewpoint a dozen or more great flames of fire extending into the skies from the wasteful burning of natural gas. Now the pipe lines are extending farther and farther into the remoter counties and even into the adjacent states to furnish a diminishing supply of this gas in an effort to meet the increasing needs of the community.

Such shameful waste of resources is thoroughly discreditable to a great state. The only reasonable explanation of its having

been allowed is the fact that during the past century Pennsylvania and other states have been so in earnest in their endeavors to bring about material development that they have naturally lost sight of the waste problems. But this can no longer be a rational explanation. As a great state already well developed, with a population and wealth ranking second among the great states of the Union, this development has already reached a stage at which problems of conservation demand comprehensive action on the part of the State.

During the past few years there has been a notable awakening in this country in behalf of the inauguration of plans and practices such as will make for greater safety and efficiency in the utilization of the country's resources, and much has been accomplished in bringing about a recognition of the right and the duty of both the state and the nation to safeguard the permanent welfare of the people through the inauguration of safer and less wasteful methods in developing and using the mineral wealth of the country.

It may, therefore, be of interest to the students of Lehigh University to consider briefly the progress which has been made in that direction; the need of further progress; and the relations of the national Government thereto.

In the matter of inspection looking to the prevention of mine accidents the states have made commendable progress. The State of Pennsylvania has a central Department of Mines at Harrisburg, and under this Department of Mines it has twenty district inspectors in the anthracite region, and 21 or 22 inspectors in the bituminous coal fields. These men have rendered important service to the State. In the other coal mining states there are some ninety inspectors, including ten in Illinois, thirteen in Ohio, and thirteen in West Virginia. The states of Virginia, Oregon, Idaho, California, North Carolina and Georgia have a small coal production, but so far as known, have no adequate inspection.

The majority of the metal mining states provide some inspection, but the inspection in the metal mines is generally far less systematic and efficient than that in the coal mines.

Some of our earlier statesmen held the theory that the func-

tion of government should be restricted to the protection of life, liberty, and property. They were inclined to regard the general welfare clause in the Federal Constitution as an invention of the devil or of some kindred spirit, and as an unfortunate insertion in that document. But the importance of this clause in connection with our national development is doubtless fully recognized and appreciated by all who are more or less familiar with governmental scientific researches on behalf of the public health and safety, of transportation, and of agriculture, mining and other industries—all of which are more or less dependent upon this clause for constitutional warrant and authority.

For any future readjustment of existing legislation and court decisions concerning the relations of the general public to the ownership and control of resources essential to the proper development of the nation under the existing Constitution, we must depend upon an increasingly liberal interpretation of this general welfare clause, supplemented by increasingly liberal sympathetic interpretations of those clauses in the Constitution which concern the regulation of interstate commerce and property rights of citizens.

Recent state legislation and decisions of the Supreme United States Courts throw some light upon development in this direction:

Thus, in 1908, the State Senate of Maine submitted to the Supreme Court of that State an inquiry "as to the right of the legislature to restrict the cutting of trees on private land for the prevention of droughts and floods, the preservation of the natural water supply, and the prevention of the erosion of such lands, and the consequent filling up of rivers, ponds, and lakes."

In its decision rendered March 8, 1908, the Supreme Court of Maine sets forth "two reasons why the right of the public to control and limit the use of private property is peculiarly applicable to property in land," as follows:

"First, such property is not the result of productive labor, but is derived solely from the State itself, the original owner; second, the amount of land being incapable of increase, if the owners of large tracts can waste them at will without State restriction, the State and its people may be helplessly impoverished and one

great purpose of government defeated. . . . We do not think the proposed legislation would operate to 'take' private property within the inhibition of the Constitution. While it might restrict the owner of wild and uncultivated lands in his use of them, might delay his taking some of the product, might defer his anticipated profits, and even thereby might cause him some loss of profit, it would nevertheless leave him his lands, their product and increase, untouched, and without diminution of title, estate, or quantity. He would still have large measure of control and large opportunity to realize values. He might suffer delay but not deprivation. . . . The proposed legislation . . . would be within the legislative power and would not operate as a taking of private property for which compensation must be made."

In 1905, the State of New Jersey enacted a statute which made it unlawful for any person or corporation to transport or carry through pipes the waters of any fresh water lake, river, etc., into any other state for use therein. In approving the constitutionality of this statute, the Supreme Court of the United States had this to say:

"The fresh water lakes, ponds, brooks, and rivers, and the waters flowing therein constitute an important part of the natural advantages of the State, upon the faith of which its population has multiplied in numbers and increased in material welfare. The regulation of the use and disposal of such waters, therefore, if it be within the power of the State, is among the most important objects of government."

Still more far-reaching was the conclusion of the court, in this case, that—

"We are of the opinion, further, that the constitutional power of the state to insist that its natural advantages shall remain unimpaired by its citizens is not dependent upon any nice estimate of the extent of present use or speculation as to future needs."

Along the same line are the interpretations of state statutes enacted to prevent the waste of gas and oil. While these decisions are not so suggestive as those above noticed, yet they show that a state may prevent the waste of an article in which any

considerable number of citizens may have a common ownership. Thus, for example, on May 18, 1893, the State of Indiana enacted a statute which prohibited any one having control or possession of any natural gas or oil well from permitting the gas or oil therefrom to escape into the open air. The Ohio Oil Company, in boring for oil in Indiana, claimed inasmuch as it was boring for and transporting oil, the escape of the gas was a necessary preliminary or accompaniment and that the state had no constitutional right to interfere; more especially because of the fact that this oil was intended for transportation into another state, and that the activities of the company were, therefore, protected against interference by the State under the interstate commerce clause of the Constitution. The Supreme Court of the United States, referring to this statute, said it was constitutional, on the principle that—

“The right of taking the gas . . . was common to all owners of the surface, and because of such a common right in all land owners, an unlimited use by any, it was competent for the State to prohibit. This limitation upon the surface owners of property was justified by the peculiar character of gas and oil, they having the power of self-transmission, and that therefore to preserve an equal right in all surface owners there could not be an unlimited right in any.”

The statute was one of true conservation, securing the rights of property, not impairing them. Its purpose was to secure to the common owners of the gas a proportionate acquisition of it.

This and other recent decisions by the Supreme Court have fixed clearly the constitutional right of the state to regulate the extraction of gas and oil from the earth, and to prevent the waste of gas and oil in connection with their extraction. But these decisions are based upon the nature and mode of occurrence of gas and oil, namely, that they permeate or occupy strata extending under large and uncertain areas; and that any person or persons in extracting gas or oil from any portion of such area or areas may, and probably would, draw supplies of oil and gas from areas beyond those which they own or control.

Under the decision of the Supreme Court sustaining the validity

of the Indiana statute, it is not clear though probable that the court would go further and uphold the constitutional right of a state to interfere or prevent the wasteful methods of mining coal and other mineral substances, which do not possess the power of "self-transmission," unless, of course, there was a common ownership, or a right in many to resort to a common supply.

Thus far, state legislation looking to the prevention of waste of natural resources appears to have been limited to forests, water, oil, gas, fish and game; and the constitutional right of the state to interfere on behalf of conservation in such cases has been upheld by the Supreme Court of the United States.

No state except Wisconsin (and possibly California) has enacted legislation which has for its purpose the prevention of waste in the mining and treatment of coal and other mineral substances which do not possess what the Supreme Court calls the power of self-transmission. Read Wisconsin Act.

CHAPTER 143

AN ACT to create section 4570m of the Statutes, to prevent the unreasonable wasting or the malicious injury, destruction, or impairment of any natural resource.

WHEREAS, The unreasonable wasting or the malicious injury, destruction, or impairment of any natural resource is inimical and detrimental to the general public welfare, therefore

The people of the state of Wisconsin, represented in senate and assembly, do enact as follows:

SECTION 1. There is added to the statutes a new section to read: Section 4570m. 1. It is hereby made unlawful for any person, firm, or corporation, unreasonably to waste or maliciously to injure, destroy, or impair any natural resources within this state.

2. It is the purpose of this act to promote and secure the conservation of the natural resources within the state in the interests of the public welfare.

3. Any person, firm, or corporation violating the provisions of this act shall be deemed guilty of a misdemeanor and upon conviction thereof shall be punished by a fine of not more than

fifty dollars, and for a second offense may be punished by a fine of not more than two hundred dollars.

SECTION 2. This act shall take effect and be in force from and after its passage and publication.

Approved May 12, 1911.

It is believed from the decision of the court in the New Jersey case of the Hudson Water Company vs. McCarter, and other decisions quoted above, that the Supreme Court would sanction as constitutional any proper statute on the part of the state with such object in view.

This belief gains encouragement from the development of public opinion concerning the nature of property rights in the present day meaning of the Federal Constitution. The decision of the Supreme Court of Maine, in the case referred to above, mentions certain property rights as not being "the result of productive labor, but is derived solely from the State itself, the original owner"; and as being distinct in important respects from property rights gained as a result of productive labor. There has been a recent tendency in other courts to draw a similar distinction. Thus, in handing down the decision of the New York Court of Appeals, in the case of the People v. New York Carbonic Acid Gas Company, November 23, 1909, which held that the State of New York had a right to interfere to prevent the waste of mineral water, Justice Gray expresses the following opinion:

"The adoption of this doctrine of a reasonable use of one's property in subterranean percolating water, to be measured by the rights and necessities of others, as a modification of the earlier rule, obviously resulted from a consideration of the differing conditions of the age, and of the possibilities of an unlimited and destructive use from modern engineering methods."

But Mr. Chief Justice Cullen of the same court, while concurring in the decision of the court, recorded the following as expressing his opinion concerning the property rights and the right to waste such property and unfortunately it represents a widely prevailing opinion—as follows:

"A man owning the coal mine" may mine the coal and waste it, regardless of the interest of the present generation or of succeed-

ing ones. It is not that such conduct would not be an evil, but because the people who framed our system of government, taught by experience, deemed it wiser to trust the use of property to the dictates of the intelligent self-interest of the owner rather than to subject it to governmental interference."

Certainly there is need of further progress and reform in our fundamental classification of property rights. The time was when a man *owned* his servants, to do with as he chose; but that is not true today in any civilized country. And the Supreme Court of the State of Maine, in drawing the distinction between property which *is*, and property which *is not*, the result of productive labor, may furnish a basis for a further useful classification that will enable a state to protect from wanton and unnecessary waste such natural resources as coal and oil and gas; which have required long ages for their accumulation; of which there is but the one supply; which are absolutely essential to both the future and the present welfare of the nation; which, as they are used, are completely destroyed and cannot, therefore, be used again; and which, in spite of all these facts, we are wasting in the United States to-day to an extent and in a manner that are a discredit to any civilized community.

Another important question in connection with the conservation of mineral resources for the exclusive benefit of the State in which they occur, was decided by the United States Supreme Court on May 15, 1911, against the exercise of such right by a state. The State of Oklahoma enacted a statute, approved December 21, 1907, which prohibited the laying and maintaining of gas pipe lines for the transmission or transportation of natural gas from the State of Oklahoma, across its boundary line, into other states and claimed the right to do this under the Constitution. The representatives of the State claimed in connection with this legislation "the right to conserve, or rather the right to reserve, the resources of the State for the use of the inhabitants of the State, present and future . . . , the ruling principle of the law being conservation, not commerce."

The Supreme Court of the United States, in construing this Oklahoma statute, conceded the right of the State to preserve the supply of gas;—It might prohibit or regulate its use, or for-

bid its waste;—but the court said that the provisions of this particular statute were not directed against the *waste* of the gas, but against *any use* of the gas, *except within the State of Oklahoma*. The court further declared, and it is to this declaration that I desire to call special attention, that—

“In such commerce, instead of the States, a new power appears and a new welfare, a welfare which transcends that of any state. But rather let us say it is constituted of the welfare of all of the states, and that of each state is made the greater by a division of its resources, natural and created, with every other state, and those of every other state with it. This was the purpose, as it is the result, of the Interstate Commerce clause of the Constitution of the United States.”

The court suggestively adds “if there is to be a turning back, it must be done by the authority of another instrumentality than a court.” In a country where private rights have so often been in the ascendancy it is refreshing to have from a court a decision placing the welfare of the community above that of the individual, and the welfare of the nation above that of the community. Such a court should not be recalled.

The police regulations for mining operations in the several states are clearly within the province of the states and not the Federal Government, as set forth by the framers of the Constitution. But as Senator Root said in a notable address delivered in New York, November 23, 1909:

“Interdependence of life, wiping out State lines, the passing to and fro of men and merchandise, the intermingling of the people of all sections of our country without regard to State lines, are creating a situation in which from every quarter of the horizon come cries for Federal control.”

The lack of uniformity in our State mining laws; the difficulty in getting one state to enact and enforce rigid regulations for safeguarding the lives of miners and for preventing waste of resources, because that state would be thereby placed at a disadvantage under such restrictions in its competition with the mining in another state not adopting such restrictions; and other conflicting interests and conditions keep this agitation somewhat active.

But the taking on of such additional functions by the Federal Government would not only be out of accord with the existing spirit of the Constitution; but it will be unnecessary if the sovereign States will exercise the powers reserved to them to do their full duty and would act in accordance with the fact that no modern day State can "live unto itself alone," but all must cooperate for the common good.

It has been suggested in this connection that the Federal Government might cooperate with the States in behalf of safeguarding the lives of miners and preventing waste of resources by prescribing certain conditions which must be followed in the future working of the mines on property still owned by the Federal Government, leaving the States to so regulate such mining operations as will meet these requirements.

In the case of the United States vs. Gratiot before the U. S. Circuit Court in Illinois, June, 1839, involving the power of the President to lease lead mines, it was decided, and this decision was later affirmed by the U. S. Supreme Court, that the Federal Government not only had the right to lease its mines on the public lands, but it also has—

"the right to stipulate with the lessee, as one of the conditions of his lease, that he shall sell the ore he digs, or the lead he manufactures, at a fixed price."

In the working of the mines on lands belonging to the Indians and which are still under Government supervision, the Government may prescribe such conditions; and in the operation of the mines in the Territory of Alaska, the Government may not only prescribe rules and regulations, but is entrusted with the police supervision in mining operations.

The right of the Federal Government, under the general welfare clause of the Constitution, to appropriate means and to conduct investigations such as may throw light upon the importance of these problems, and discover how these resources can be extracted with minimum loss of life, with minimum waste of resources, and with maximum economy in cost and labor. By gaining this information and properly placing it before the American public, the Federal Government will appear to have

discharged its clearest duty in relation to the mining operations of the country.

In the days when our Constitution was framed, the conditions then existing were radically different from those of today. The functions of the Federal Government of that day might well have been limited largely to the protection of life, liberty, and property. At that time we had no mining industry. Today we have a mining industry, the greatest and most complex in the world; we have factories and varied industries distributed over an area nearly ten times that of the original thirteen states, which factories and industries are largely dependent upon this mining industry; we have this great area traversed by an elaborate system of steel railroads, built and operated by means of products of the mines; which products also make up over sixty per cent of the total freight transported. It is over these railways of steel and in our steel ships that we transport our mails, our commerce, our army, our navy, and by means of which people intermingle for private and public welfare, independently of state boundary lines.

With the increasing density of population and the larger development of the country's resources, the interstate relations in agriculture, mining, manufactures, transportation, and the varied industries have grown in extent and complexity far beyond the dreams of our forefathers. The ore mined in one state, mixed with the coal from another, and the limestone from a third, is, in still a fourth, manufactured into steel for the construction of bridges and houses to be built and used in each and all of the states. The coal from Pennsylvania and West Virginia furnished light and heat and power in the cities and factories of New England; just as the mines of Western Pennsylvania, Ohio and Illinois furnish heat and light and power for cities in the far North West and down the Mississippi River to the Gulf. Our old time concern and anxiety as to the relations between domestic states has largely given place to the wider concern and deeper anxiety regarding our relations as a nation with the world's other great nations.

This great system of national life and industry in the United States of today has long since surpassed the most sanguine hopes

and anticipations of the framers of the Constitution; and it goes without saying that the Constitution should and will be interpreted and changed, as need be, to keep pace with this phenomenal growth and to meet our larger and more complex national and international relations.

The two foundation industries of this great national life are *agriculture*, which produces our food supply and clothing; and *mining*, which furnishes heat and light for the nation, contributes more than 60 per cent of the total freight tonnage of the country, supplies the materials from which our buildings, railways and ships are constructed and upon which many of our factories operate, and generates the power which turns the wheels of industry and moves the trains and ships of commerce.

Only a few weeks ago the English people awoke to the fact that the closing of their coal mines threatened not only the industries, but the transportation and food supply,—indeed the very life of the nation. They found themselves unexpectedly face to face with what Lord Cecil pronounced the most serious crisis of that country within the memory of living men; and which the Prime Minister said was a crisis that threatened the very life of the nation.

The British Government found itself entirely without information concerning those details of the mining industry which would serve as a basis for framing appropriate, immediate, legislation, and it was impossible to obtain that information under the prevailing conditions and within the available time. As a result of this lack of information, and the complexity of the situation Parliament framed and has made operative an emergency legislative measure that is satisfactory neither to the Government nor to the opposition, to the miners nor to the operators. Now that the crisis has been tided over for the time being, it is understood that the British Government will initiate a most thorough examination into all the conditions obtaining in the coal mining industry.

In the United States also, where both internal and external conditions, and national and international relations, are developing unexpectedly, and changing without warning, we should not only see to it that each of the forty-eight sovereign states per-

forms its own and its full duty in behalf of the efficient development and wise use of our mineral resources, and in behalf of the men who daily face the hazards of the mining industry; but we should none the less see that the National Government meets its full responsibilities and discharges its full duty toward the accomplishment of the same purposes, safeguarding thereby its own permanent welfare, especially in the way of conducting needful inquiries and investigations such as will prove helpful to the wise development of the industry in all the states.

Already the Federal Government has authorized certain investigations. The Geological Survey, cooperating with similar organizations in the several states, has made extensive and important contributions to our knowledge concerning the nature and extent of the varied mineral resources and topography in different parts of the country.

The new national Bureau of Mines, inaugurated July 1, 1910, has for its general purpose and function the conducting of inquiries and researches concerning the mining, treatment, and utilization of mineral substances, with a view to improving health conditions and increasing safety, efficiency, economy, and the prevention of waste in the mining, quarrying, metallurgical and other mineral industries. It will encourage individuals and corporations to conduct at their own expense investigations which are purely local and individual. It will encourage the States to conduct at their own expense such investigations as are local to their own needs. It will endeavor, as authorized by Congress, to conduct inquiries and investigations which are general and national in character and importance, and which will be useful to each of the states in its police legislation looking to the safeguarding of the lives of the miners and the prevention of a waste of the country's resources; and it will endeavor to aid all who are engaged in the industry to develop a safer and more efficient utilization of these resources. The Bureau should also be able to furnish to the Federal Government information concerning the utilization of these resources that will enable this government to plan and to facilitate such use of these resources in the country's international relations as will best facilitate our national progress.

This general plan, it is believed, will encourage each individual and each State to bear its part of the burden; and will avoid the extensive duplication in cost and effort which would result if the different states and individuals undertook to conduct the separate investigations, both special and general. It will likewise keep down the burden of cost which would otherwise fall on the Federal Government, in case that government should undertake to conduct all these investigations, both local and general.

The scope and completeness of these investigations, however, are as yet inadequate for the immediate needs of the situation.

In conclusion, I must not fail to call attention to the fact that it is quite possible for the National Government to affect the mining industry injuriously. In 1884, the United States Circuit Court in California, by an injunction issued under a Federal statute, and without granting a delay sufficient to bring about any readjustment of economic conditions, stopped the placer mining industry in California and rendered inactive property valued at not less than \$100,000,000. Since that unfortunate occurrence the Federal Government has conducted no inquiry or investigation looking to the reestablishment of that industry, which it helped to destroy by a court injunction.

A general law now upon the statute books, by preventing practical cooperation among the coal operators of the country, has developed a destructive competition among these operators, and is today in a measure responsible for the present discreditable waste of coal and loss of life in our coal mining industry.

In conclusion, I can not too earnestly impress the fact that the wise future use of the nation's resources, and the best progress of our great mining industry will depend largely upon the clearness with which the matter is understood, and the patriotic determination with which the situation is mastered and improved by the chemist and engineers of today.

HYDROMETRIC WORK OF THE UNITED STATES GOVERNMENT

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Hydrometry is interpreted as the measurement of the quantity of water as precipitation, run-off, ground water, and evaporation. Water measurements are made by the Corps of Engineers, U. S. Army, the Weather Bureau, Bureau of Experiment Stations, the Forest Service of the Department of Agriculture, the Geological Survey, Reclamation Service, and Office of Indian Affairs of the Department of the Interior, and certain intensive work is performed under the authority of the National Forest Reservation Commission.

Measurements of precipitation are made by the U. S. Weather Bureau. The work was begun in 1871, and there are at present about 3500 stations in the United States. Some portions of the West, especially in the higher mountain regions, are not well covered by precipitation measurements. Snowfall observations, or the water equivalent thereof, are made by the Weather Bureau, but the work is not as satisfactory, nor as widespread as the measurement of rainfall. A summary of the precipitation data collected by the Weather Bureau from 1871 to 1909 has been published as Bulletin W, Climatological data by sections.

Run-off measurements are for the most part made by the U. S. Geological Survey. The work is well distributed over the entire country. It began in 1888 under an Act of Congress providing for an investigation of irrigation possibilities in the public lands of the West and was extended in later years. The distribution of the gaging stations and the titles of the reports containing the data are given in Water-Supply Paper 280, of the Geological Survey.

A large area in the United States has been examined for ground water resources by the Geological Survey, and the work is well in progress. Not only have artesian basins been defined and their capacities determined, but in many places in the arid West, the ground water levels have been studied and the effect thereon of continued draughts for irrigation purposes has been shown. In the East as well as in the West, the investigations of ground water have furnished to individuals and to smaller cities and towns desired information concerning the possibility of securing ground water for municipal and domestic supplies. The locations in which these investigations have been performed are given in Water-Supply Paper 280, above described.

Evaporation measurements have been made in many places throughout the United States by the Geological Survey, the Weather Bureau, and several bureaus of the Department of Agriculture. The results of the work are not as satisfactory as are those of the measurement of precipitation and of run-off. The most important work in the determination of evaporation has been performed by the Weather Bureau at the Salton Sea in Southern California. A full report on the entire subject of evaporation is now in preparation.

PREVENTION AND CONTROL OF FOREST FIRES

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It may be asked what connection there is between chemistry, most venerable of sciences, and the younger art of forestry; in reality there are matters of great import which they have in common. Of all events, excepting great volcanic eruptions, forest fires are most widespread in their chemical and physical effects. They alter the soils, pollute the atmosphere, and change the character of streams. Their realm embraces all the ancient elements;—Fire, Earth, Air and Water.

Chemistry, properly applied, works for our health, comfort and contentment. Our bodies, together with the food, raiment, and shelter which they need, come from the earth, and they must have a constant supply of water, or they die. Between the animal and vegetable kingdoms an equilibrium exists. Plants decompose the poisonous exhalations of animals and liberate into the atmosphere the oxygen and ozone. It is not extreme to say that the removal of a large part, either of plants or animals, would compel the surviving kingdom to modify its mode of existence, and that this would not be to its advantage.

Nearly all of the food crops are sown and harvested by man, but in the forests of the United States man reaps where he has not sown. This, on the face of it, foreshadows a danger. Through some of the operations of man, inspired by greed, there has been caused a great scarcity of wild pigeons, buffalo, salmon, seal, and other forms of life; and the rubber, quinine, and cascara, and other forms of plants. Such operations are wrong, since all natural resources, except mineral, can be used in such a manner that the supply may be maintained instead of depleted. In this line of thought, Forestry is the plow-point of Federal progress. It challenges the best there is in us towards the fulfillment of a Higher Patriotism, and the recognition of the Higher Law.

The prevention and control of forest fires are questions of great importance. In the United States, on an average each year, seventy human lives are lost; 10,000,000 acres are burned; at least \$25,000,000 worth of timber is destroyed; and there are other losses which can not easily be expressed in dollars, resulting from the destruction of young growth, the impairment of water-sheds, and the interruption of business, to say nothing of mental depression and the lowering of the moral tone. We cannot afford this useless waste, and it is in recognition of this fact that the Congress has established and maintained the Forest Service for the protection and administration of National Forests.

A critical inquiry into the causes of forest fires naturally precedes the inauguration of preventive measures. It appears that all forest fires, excepting those resulting from lightning or spontaneous combustion, are preventable where the causes are known. They are due to ignorance, carelessness, or maliciousness, and if they are to be prevented it will be necessary to teach the ignorant, restrain the careless, and reform the malicious. This is the duty of all good citizens, and in this duty the Forest Service has taken the lead.

Some conclusions may be drawn from reliable statistics of forest fires on the National Forests which show causes as follows:

| | Per cent |
|----------------------------------|----------|
| Railroad locomotives..... | 27 |
| Unknown..... | 21 |
| Lightning..... | 17 |
| Campers..... | 15 |
| Miscellaneous..... | 9 |
| Brush burning..... | 5 |
| Incendiary..... | 5 |
| Sawmills and donkey engines..... | 1 |
| | <hr/> |
| | 100 |

The classification of these cases is according to a scheme which may be outlined as follows:

CLASSIFICATION OF THE CAUSES OF FOREST FIRES

The heavy face type shows the terms used in reporting the causes of fires

| | |
|--|--|
| Intentional INCENDIARY Maliciousness, or wilful negligence. Content for the law. To cover crime. To drive game. | Includes all fires that are intentionally set or due to willful negligence but not those due to carelessness, mischief or ignorance. "Intentional," however, does not include back-burning with good intent, which is classed according to the origin of the fire being fought. |
| RAILROADS Passenger, freight, and work engines. Steam shovels and plows. Logging engines. | Includes all fires caused by sparks or ashes from traction locomotives, but not from clearing of rights-of-way, which are reported under brush-burning. |
| SAWMILLS Permanent mills. Temporary mills. Portable mills. Donkey engines. | Includes sparks from stationary engines, but not fires from logging locomotives nor from loggers while slashing, clearing, cooking or river-driving. |
| SPARKS OR ASHES FROM ENGINES Preventable Caused by man. | Includes all fires incidental to the removal of litter or undesirable growth, unless willful negligence is evident, in which case it is "incendiary." |
| BRUSH BURNING Clearing lands or rights-of-way. Slash, rubbish or garbage burning. Shabbel or meadow burning. Light burning. | Includes fires due to carelessness, mischief or ignorance, and fires started by Indians, but not fires started to drive game or to increase the grazing area. Such are "incendiary." |
| CAMPERS Construction campers. Recreation parties and picnickers. Fourth of July parties. Miners and prospectors. Hunters and fishermen. Stockmen, including branding and protection fires. Berry pickers and nut gatherers. Cruisers, surveyors, and river drivers. Smokers, children, tramps, drunks, lunatics. | MISCELLANEOUS Fires from burning buildings or from prairie or other fires, if the origin of the original fire is not known. If origin can be determined it is classified accordingly. Sparks from chimneys and stacks, other than those classified under RAILROADS and SAWMILLS. Blasting, except as covered by the classification "BRUSH BURNING." From electric wires, unless accompanied by lightning. Spontaneous combustion, either chemical or mechanical. |
| Forest fires Unintentional Generally from Uncontrolled Fires. | UNKNOWN Includes fires the cause of which is not determinable with reasonable certainty. |
| Generally unpreventable | LIGHTNING |

On a casual study of this analysis of causes it will be seen that the greater number of forest fires may be prevented by education, by law, and by good forest management. Spark arresters can lessen, or wholly eliminate, the danger from railroads and saw-mills. Brush-burning can be done at seasonable times and in a manner that creates no special hazard. Campers are not, as a rule, wanton or malicious. Incendiarism will cease when full punishment is absolutely certain. Public sentiment becomes stronger year by year and the advocates of conservation find that their teachings are accepted. The lightning alone is quite unaffected by rules, regulations, or threats.

There are plenty of laws,—too many of them,—and many of them are ineffectual, but they show that the law-makers have in some degree responded to public sentiment. The kinds of legislation in the various States is shown on the accompanying table, but of course it is impossible to indicate the value of any act.

Some indication of the awakening of public sentiment is shown by the advance in forest education and in forest legislation. Seventy-six colleges and schools now offer courses in forestry, and one hundred forty-eight schools teach forest or tree-study. In the agricultural high schools and in one-half of the normal schools forestry is taught in connection with agriculture.

The Forest rangers and guards constitute the principal patrol of the National Forests. They post printed fire warnings along the roads and trails and caution travelers regarding the danger from fires and the penalties for setting them. These officers exercise a supervision over persons within the Forests, and not only warn those who might be malicious or careless, but they preach the gospel of conservation to those who are ignorant.

All big fires start from small fires. Some small fires creep slowly over the ground; others burn only the lower vegetation. Others consume underbrush, litter, and young trees, and scorch the larger trees. Under certain conditions they may ignite the crowns of the larger trees and a general conflagration follows. It is evident, therefore, that there is less hazard from fire in a clean forest than in one in which the forest floor is covered with inflammable material. Under wise forest management, in which

certain trees are selected for removal together with the inflammable slash and litter, not only is a crop harvested, but the forest is left in safer condition. Thus lumbering, which heretofore has been a menace to the forest, may be turned into a benefit. The same is true of the practice of grazing stock which, when unrestricted, is ruinous to the forest floor and reproduction, but under proper management can be made to decrease the fire hazard without appreciable damage to the forest.

The application of such commonsense principles does not work a hardship upon the people nor prevent the development of legitimate business. By careful management on the National Forests the number of cattle, horses and sheep has been increased, while the carrying capacity of the wild range has also been increased. During 10 years the area required for grazing one unit has been decreased from eighty-eight acres in 1901 to forty-six acres in 1911, the unit being one cow, or horse; five sheep; or two-and-a-half hogs.

The increasing settlement and use of the National Forests has a tendency to increase the number of fires, but the relative danger from great conflagrations is decreasing, owing to the effective patrol. Moreover, the settlers assist in fire-fighting. The efficiency of the Forest Service is shown by the fact that since it has had charge of the National Forests seventy per cent of all fires have been extinguished before five acres were consumed. Of course, there will always be times when, owing to drouths and high winds in a region where the forest is very inflammable, it would be impossible to bring a large fire under control. Such a case was the Great Idaho Fire of August 1910, in which seventy-six employees lost their lives.

Although maliciousness, carelessness, and ignorance are steadily on the decrease, it will, unfortunately, be many years before they will be obliterated, and, therefore, the control of forest fires will continue to receive special study. Moreover, fires will always be caused by lightning. The first and most important measure is a vigilant patrol by forest rangers and guards, and the establishment of lookout stations at high points, commanding a large expanse of country. These stations are equipped with telescopes and other instruments for discovering smoke and deter-

STATE LEGISLATION RELAT-

Including the Legislative

(x indicates

| State | Forest Fire Protective System | Fire Fighting | | Liability of Individuals, Corporations, or Others for Causing Fires | |
|------------------------|-------------------------------------|--|-----------------------------------|---|----------|
| | | Citizens May Be Called Upon to Aid | Penalty for Refusing to Aid | Civil*** | Criminal |
| 1 Alabama..... | x | x | .. | .. | x |
| 2 Arizona..... | .. | .. | .. | x | x |
| 3 Arkansas..... | .. | .. | .. | x | x |
| 4 California..... | x | x | x | x | x |
| 5 Colorado..... | x | x | x | x | x |
| 6 Connecticut..... | x | x | x | x | x |
| 7 Delaware..... | .. | .. | .. | x | x |
| 8 Florida..... | .. | .. | .. | .. | x |
| 9 Georgia..... | .. | .. | .. | .. | x |
| 10 Idaho..... | x | x | .. | x | x |
| 11 Illinois..... | .. | .. | .. | x | x |
| 12 Indiana..... | .. | x | .. | x | x |
| 13 Iowa..... | .. | .. | .. | x | x |
| 14 Kansas..... | .. | .. | .. | x | x |
| 15 Kentucky..... | .. | .. | .. | x | x |
| 16 Louisiana..... | x | .. | .. | x | x |
| 17 Maine..... | x | x | x | x | x |
| 18 Maryland..... | x | x | x | x | x |
| 19 Massachusetts..... | x | x | x | x | x |
| 20 Michigan..... | x | x | x | x | x |
| 21 Minnesota..... | x | x | x | x | x |
| 22 Mississippi..... | .. | .. | .. | x | x |
| 23 Missouri..... | .. | .. | .. | x | x |
| 24 Montana..... | x | x | x | x | x |
| 25 Nebraska..... | .. | .. | .. | x | x |
| 26 Nevada..... | .. | .. | .. | x | x |
| 27 New Hampshire..... | x | x | x | x | x |
| 28 New Jersey..... | x | x | x | x | x |
| 29 New Mexico..... | .. | .. | .. | x | x |
| 30 New York..... | x | x | x | x | x |
| 31 North Carolina..... | .. | .. | .. | x | x |
| 32 North Dakota..... | .. | x | .. | x | x |
| 33 Ohio..... | .. | x | x | x | x |
| 34 Oklahoma..... | .. | .. | .. | x | x |
| 35 Oregon..... | x | .. | .. | x | x |
| 36 Pennsylvania..... | x | x | x | x | x |
| 37 Rhode Island..... | x | x | x | x | x |
| 38 South Carolina..... | .. | x | x | x | x |
| 39 South Dakota..... | .. | .. | .. | x | x |
| 40 Tennessee..... | x | x | x | x | x |
| 41 Texas..... | .. | .. | .. | .. | x |
| 42 Utah..... | .. | .. | .. | x | x |
| 43 Vermont..... | x | x | x | x | x |
| 44 Virginia..... | .. | .. | .. | x | x |
| 45 Washington..... | x | x | x | x | x |
| 46 West Virginia..... | x | x | x | x | x |
| 47 Wisconsin..... | x | x | x | x | x |
| 48 Wyoming..... | .. | .. | .. | x | x |

* Prepared by the Office of State Cooperation.

** This table shows merely in what states there is any legislation whatever along the lines indicated, irrespective of the extent of such legislation.

*** In the absence of any specific legislation by a State on the subject of such civil liability, the parties injured

ING TO FOREST FIRES

Sessions of the Year 1911*

legislation**)

| Burning Brush, Grass, etc., for Agricultural or Pasturage Purposes | | | Protective Measures Concerning Clearing Rights of Way, Patrol, Spark-Arresters, Slash Disposal, etc., Applying to Railroads, Lumbermen, and Others | Specific Appropriation for Fire Protection |
|--|---------------------|------------------------------------|--|--|
| Closed Season for Burning | Permission Required | Notice to Neighbors Before Burning | | |
| x | .. | x | x | 1 |
| .. | .. | .. | .. | 2 |
| .. | .. | x | .. | 3 |
| x | x | .. | x | 4 |
| .. | .. | .. | x | 5 |
| x | x | .. | .. | 6 |
| x | .. | x | x | 7 |
| x | .. | x | .. | 8 |
| x | .. | x | .. | 9 |
| x | x | .. | x | 10 |
| x | .. | x | x | 11 |
| .. | .. | .. | .. | 12 |
| x | .. | .. | .. | 13 |
| x | .. | .. | .. | 14 |
| .. | .. | .. | x | 15 |
| x | .. | .. | x | 16 |
| x | .. | .. | x | 17 |
| .. | .. | .. | x | 18 |
| x | x | .. | x | 19 |
| x | x | x | x | 20 |
| x | x | x | x | 21 |
| .. | .. | .. | .. | 22 |
| .. | .. | .. | x | 23 |
| .. | .. | x | x | 24 |
| x | .. | x | x | 25 |
| .. | .. | x | .. | 26 |
| x | x | .. | x | 27 |
| .. | x | .. | x | 28 |
| .. | .. | .. | x | 29 |
| x | x | .. | x | 30 |
| .. | .. | x | .. | 31 |
| x | .. | x | x | 32 |
| .. | .. | .. | x | 33 |
| .. | .. | x | .. | 34 |
| x | x | .. | x | 35 |
| x | x | .. | x | 36 |
| x | x | .. | .. | 37 |
| .. | .. | .. | .. | 38 |
| x | .. | x | .. | 39 |
| .. | .. | x | x | 40 |
| .. | .. | .. | .. | 41 |
| .. | .. | .. | .. | 42 |
| x | .. | .. | .. | 43 |
| .. | x | .. | x | 44 |
| x | x | .. | x | 45 |
| .. | .. | .. | .. | 46 |
| x | x | .. | x | 47 |
| .. | .. | .. | x | 48 |

tive of the relative value of the legislation in the several States.
have the usual common-law right to an action for damages done by fires.

mining its direction and distance, either singly or in cooperation with another similar station. Immediately on the discovery of a fire the alarm is given by telephone, heliograph, or by any other method with which the particular station is equipped.

The Supervisor, being advised of the location of a fire, is able to dispatch a crew of fire-fighters to the threatened point, and to follow this immediately with provisions and other supplies if it appears that the fire will be difficult to extinguish. It is necessary, therefore, that there should be lines of communication, roads, trails, or open fire lanes over which wagons or pack-horses may pass to reach the site of the fire. The National Forests are all upon high divides in the wildest and most inaccessible portions of the country and the few roads which originally traversed these regions were wholly inadequate for use in fire-fighting. It has, therefore, been necessary to construct and maintain additional lines of communication. During the past five years the Service has constructed 1,385 miles of roads, and 15,041 miles of trails, and as work will continue from year to year, the efficiency of the men will increase in proportion.

Fire fighting is serious business. Usually it devolves upon one man or a small body of men to extinguish a fire, since it should be attacked as soon as possible, before it reaches great proportions. This is particularly true in areas where there is much inflammable undergrowth, or where the forest is without openings which may be used as vantage points, or streams which serve to check the progress of the fire. Highways, such as railroads and roads, offer excellent lines of defense, and fire lanes are often cleared for the same purpose.

Methods of fighting fires vary according to the nature of the country and the type of forest, though there are some general features which pertain to all fires. For instance, they burn more rapidly up-hill and with the wind, and generally die down somewhat at night. Naturally the crest of a hill is the best line at which a fire may be stopped or from which back-fires might be started.

The fire-fighter seldom has water available. Sometimes wet blankets or gunny sacks can be used to beat out surface fires, but the greater amount of fire fighting is done by throwing sand or

earth from shovels upon the flames or by ditching or clearing a temporary fire lane, at which the fire stops for lack of fuel.

When a fire is so severe that it can not be attacked directly in front, the fighting crew sometimes work from both sides, gradually drawing together and pinching the fire out between them. Even then the danger is by no means removed. Smouldering embers may be fanned into flame by a rising wind, and it is, therefore necessary to see that a fire is totally extinguished.

Anyone who has witnessed a great forest fire, realizing the loss attending it, the labor and money expended in extinguishing it, and the danger which was experienced or averted, can appreciate why little fires should not be allowed to become big fires. If they cannot be prevented, they must be controlled. This has been recognized by private owners of woodlands; by the States on State Forests; and by the Nation on the National Forests.

There is still much misconception regarding the administrative policy adopted in connection with our National Forests. They are not protected for future use only. On the contrary, the first guiding principle in their administration is to put them to the highest use at the present time. Conservation, as a forester understands it, means the wise use of all resources by all people, and for all time.

The National Forests, which have a gross area of about 185,000,000 acres, are not uninhabited. They have a resident population of a quarter of a million, and four hundred thousand more use them for recreation during the summer months. The private lands within their boundaries aggregate over 22,000,000 acres, of which about a million and a half acres have been listed for agricultural settlement upon recommendation by the Forest Service. Since 1906, when the Forest Service took charge, timber has been sold to 25,000 persons who have cut over two billion board feet under proper regulations. Permits for the grazing of stock have been issued to the number of 165,000; a large majority of the permittees being owners of only small herds. The free use of timber has been granted to 170,000 persons who are living upon lands in or adjoining the Forests, and over 20,000 permits have been issued for special uses of lands or resources, covering more than a hundred different purposes. About fifty thousand

miners are operating under conditions most favorable to legitimate development.

Nor is the value of these Forests confined to their actual areas. Their watersheds conserve the water supply for 1,175 cities and towns; 1,266 irrigation projects; and 324 power projects. It has been estimated that they protect 15,000,000 horse power. In all of these great uses, the forests contribute to the health, comfort and contentment of man. They are worthy of protection.

THE CONSERVATION OF FORESTS BY PRIVATE LANDHOLDERS IN THE UNITED STATES

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Washington, D. C.

The first systematic experiment in practical forestry for the private owner in the United States was established by Mr. Gifford Pinchot upon the Baltimore Estate, near Asheville, North Carolina, in 1891. It was undertaken in a forest which had suffered greatly from fire, grazing, and destructive lumbering. It established the entire practicability of conservative cuttings which both improve growth, soundness and composition of the forest, and yield good money returns.

In 1898, the Forest Service, (then the Division of Forestry) issued a circular offering the advice and practical assistance of the Government to farmers, lumbermen, and others in the management of their forest lands. This offer greatly stimulated the interest of private forest owners in practical forestry, and has led to the conservative management of large forest areas in private hands. In the aggregate, however, the area of privately owned forest lands in the United States upon which an efficient form of systematic forestry is practiced is less than one percent of the total area of such lands. When we remember that forests privately owned in the United States contain four-fifths of all our standing timber, then the grave national aspect of the failure of most American private forest owners to handle their holdings conservatively may be adequately understood. Public sentiment for forest conservation in the United States grows steadily stronger; but it has not yet reached, except in isolated cases, the stage of practical application.

Forests privately owned in the United States fall into two classes—farmers' woodlots and larger private holdings, the latter being for the most part in the hands of lumbermen. The woodlots in this country have been estimated by the National Con-

servation Commission to contain 300,000,000,000 feet of saw timber, and 1,500,000,000 cords of wood, and to cover an aggregate area of 200,000,000 acres, nearly all of which is the region east of the great plains, where woodlots constitute about one-half the present forest. Woodlots consist in the main of scattered patches of original forest, from which the large timber has been cut. Their yield of saw timber is small, but they are the chief source of supply of fuel, posts, and rails, and also furnish a considerable number of our railroad ties.

Corporate holdings of forest land in the United States with the larger individual holdings contain about 1,700,000,000,000 feet of timber, which is on the average the most valuable in the United States. It will be seen therefore, that the maintenance of a sustained supply of timber in this country depends chiefly upon the way in which American lumbermen handle their forest holdings.

Several reasons have helped to retard the application of conservative forest methods by lumbermen. One is the generally high tax on lumberland; another is the failure of many states to pass and enforce good forest fire laws; another reason which is rapidly passing away, is the lack of general appreciation by lumbermen of the business advantages of conservative forest management. These invitations to destructive lumbering will be withdrawn through better state laws, and through the continuance unabated of educational work in forestry by the United States Forest Service and by the State Governments. But the chief reason why more American lumbermen do not practice forestry is because it costs more to grow timber than it brings at present stumpage prices, except for a few kinds, like White Pine, grown and sold under unusually favorable conditions.

From trifling beginnings American lumbering has grown as probably no great industry in the world's history ever grew before. Its great obstacles and its great opportunities brought pouring into its ranks men to whom obstacles and opportunities appeal; and the industry responded both to demand from without and to the impetus of active and resourceful men within. The ripe timber was there in untold billions of feet. Its market value on the stump was a song. The trees came down in ever

increasing battalions and the wood houses went up. From thirteen billion feet in 1870 we had jumped to twenty-four billion in 1890, thirty-five billion in 1900, and nearly fifty billion in 1911. Lumbering and other industries dependent wholly or mainly on wood already pay the wages of one and a half million men and women.

Along with this enormous growth has come enormous waste, much of which, notably the fearful loss through fire, was unnecessary. One-fourth of the standing timber is left in the woods or otherwise lost in logging. For forty years forest fires have cost an average each year of fifty lives and fifty million dollars' worth of timber. We began with nearly half the United States under forests. Today they cover scarcely one-fourth.

This, touching the high lights only, is the present condition of the wholesale lumber industry. It is selling lumber for sometimes a little less, sometimes a little more than it would cost to grow it, seldom for much more. Were stumpage figured at its actual value, and not at what was paid for it, few lumbermen in the United States would be making money, and many more lumbermen would be losing money. The average price paid for stumpage in the United States is below four dollars. The average cost of producing it again will not be less than six dollars. No economic reason adequately explains the difference between timber prices in the United States and in Europe. The difference in the density in population explains it only in part. But neither that nor the relation of supply to demand, is the chief cause. It lies in our failure to realize that if we are to grow timber continuously to meet our needs, its value must be reckoned by the cost of growing it as well as by the cost of logging and manufacture. Stumpage prices in the United States average less than one-fifth of the price of lumber at the mill. The value of anything which is needed is at least no less than it will cost to grow it again. We have manufactured more lumber and other forest products than we require; and we have established a consumption per capita unequaled in any other country, and approached by very few.

If the United States is to have a constant timber supply adequate to its needs, then that supply must come chiefly from pri-

vate lands in the ownership of lumbermen. In my judgment, some form of public regulation of cutting on private lands will be necessary in order to preserve what remains of our forests. In no other way as I see it, can adequate results be accomplished in time, because in no other way can the output of lumber be so regulated as to insure that the price paid for it takes into consideration the cost of growing it as well as the cost of logging and manufacture.

State regulation will not accomplish this in time. In the way stand constitutional limitations, the practical impossibility of uniform action, and many other disadvantages, such as an excessively high cost for administration, and the complications which would inevitably arise from laws in forty-six states to regulate the same interstate commerce and industry.

Every state can promote the practice of forestry by private owners through taxing forests reasonably and on a just basis, and through passing and enforcing laws for efficient fire patrol. Some states, notably Oregon and Wisconsin, have done their full duty already. But the effective regulation of lumbering on private lands is the function of that agency which can accomplish it most promptly, most uniformly and most efficiently, which is the Federal Government.

For regulation to be productive, three things are essential. It must be legal, it must be practicable, and it must be fair to the consumer of lumber, to the lumber industry and to the forest. I believe that such regulation should follow these main lines:

The owners of timber land and stumps in any forest region should be permitted to form an organization, so as to enter into a cooperative agreement with the Federal Government.

The cooperative agreement should provide, with adequate penalties for non-compliance, that all members of the Lumbermen's Organization shall log conservatively under methods prescribed by the Government, and shall protect their forest holdings from fire.

The additional cost incident to conservative logging and the expense of fire protection should be borne by the lumbermen, from an appropriation paid in by them consisting of a fixed charge of from twenty-five to fifty cents, depending on the region, per

thousand feet of lumber cut each year. For example, should the holders of Southern Yellow Pine enter into such an agreement with the Federal Government, they would expend under the direction of the Government in the cost incident to conservative logging and to fire patrol, say twenty-five cents per thousand feet of lumber cut, or about two and a half million dollars a year, on an annual cut of approximately ten billion feet.

In order to insure a continuous supply of timber from the region concerned, and to prevent over supply or under supply of lumber above or below what the forest can permanently produce, the Government, under the cooperative agreement, should be empowered to fix the output of lumber from all timber lands covered by the agreement.

The regulation of the lumber industry does not involve the public ownership of forest land. It involves a task much more difficult—the supervision of the methods and output of corporate enterprise. If it is carried out without due regard for the public interest it will defeat its object, which is to furnish wood continuously to American citizens for no more and no less than it is worth. If it is carried out without due regard for the legitimate interest of the lumber industry it will fail no less disastrously.

The statement will probably be made that the regulation outlined here would promote concentration. It would permit the forming of organizations composed of timber owners in the several forest regions, and it would simultaneously regulate their methods and their lumber product in their own and in the public interest. To those who set their faces against concentration of any kind or for any purpose in any industry, this plan will not appeal. But to those who hold that the fair and firm regulation of national industries is needed to safeguard the industrial welfare of the nation and the prosperity of the plain American citizen, this discussion of our condition and of our need as to timber may be of some interest.

A BUSINESS POLICY FOR A NATIONAL DOMAIN

*What the United States Government is doing in the classification
and valuation of its public lands.*

GEORGE OTIS SMITH,

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PRESENT EXTENT OF THE PUBLIC DOMAIN

During the half century from 1803 to 1853 the United States of America acquired lands to the extent of one and a third billion acres, another one-third of a billion acres in Alaska constituting a subsequent purchase. With this embarrassing wealth of lands, the Federal Government naturally endeavored in the following half century to dispose of its vast domain, and the problem was largely that of getting pioneers to penetrate the wilderness. Land grants were made to the newly organized States, to the transcontinental railroads, and to builders of military wagon roads, on a scale that now seems lavish, and in amounts that aggregated hundreds of millions of acres.

The earlier policy of sales logically gave place to that of settlement laws, the purpose and principle of which were the establishment of homes upon the land, the distribution of the Nation's lands among its citizens, and the creation of a class of homeowners. So, too, with the mineral lands, discovery and development were the only statutory conditions imposed by Congress as preliminary to transfer of title for the richest of mineral treasure. Thus the nineteenth century, which saw the creation of a national domain, an empire in itself, also witnessed the distribution of more than one-half of its area. With nearly 200 million acres permanently set apart as National forests and parks, there therefore now remains only about one-fourth of the original public domain, exclusive of Alaska, or approximately 325 million acres as unappropriated, unreserved public land.

The shrinkage of the national domain has naturally been coincident with the Nation's development in all lines of industry. The western prairie has become the world's granary, and what were once public lands are contributing to their private and corporate owners no small proportion of the world's output of metals and of mineral fuels. With a national growth on this scale, there has come necessarily, a general increase in land values and the problem of finding land for the settler is already looming large on the horizon. Exploration and exploitation must now be followed by intensive utilization. With the most and the best of the Nation's land already alienated, the task is to put to its best use what remains.

STATUTORY BASIS FOR LAND CLASSIFICATION

Wise utilization of lands predicates scientific classification, and indeed many of the earlier laws in recognizing classes of land presupposed classification. Thus, the statutes enacted 30 years or more ago provide that "lands valuable for minerals are to be reserved from sale or entry under the non-mineral laws," and again, that lands valuable for gold, silver, and copper can not be sold as coal lands even though beds of coal may underlie the auriferous gravels.

The first step toward providing specifically for a scientific classification was taken in 1879 when Congress, acting upon the advice of the National Academy of Sciences, made "classification of the public lands" the first of the statutory functions of the United States Geological Survey, then created as the successor to the earlier federal exploratory surveys. That this specific duty was for so long a period subordinated to the more general task of investigating the public domain and determining its natural resources, may now seem a matter of regret, yet at that time there were lacking the organized corps of trained scientists and engineers and the mass of accumulated field data that were later available for the task and absolutely essential to its accomplishment.

The present public land policy has as its keynote highest utilization, and I believe this epoch in public-land legislation

and administration may be said to date from 1888 when Congress made special provision for an irrigation survey and authorized the withdrawal or reservation, pending further legislation, of the reservoir sites and irrigable lands designated as a result of that special investigation by the Geological Survey. This legislation was simply the forerunner of the Reclamation Act of 1902, which is most notable as providing a practical means of insuring that the irrigable lands thus classified shall be put to their highest use, through a Federal agency, the construction-engineer corps of the Interior Department, known as the Reclamation Service.

The legislative history of the establishment of the National forest policy is somewhat similar. The Act of 1891 authorized executive reservations, but the thirty forest reserves thus created were areas selected on the basis of only general information, and opposition to them developed by reason of their inclusion of arable and mineral lands. The Act of June 4, 1897, which was another example of legislation based upon a recommendation of the National Academy of Sciences and marks the beginning of an effective national administration of forest lands, suspended for nine months, the latest withdrawals amounting to more than 22 million acres and provided for an examination and survey of these areas in the intervening time by the United States Geological Survey. The purpose of this examination was to determine the relative values of these public lands, in order to prevent the inclusion within forest reserves "of lands more valuable for the mineral therein or for agricultural purposes, than for forest purposes." The development of the administrative work under this act and its subsequent amendments necessitated the organization in 1905 of another technical corps, the Forest Service, under whose trained foresters the 188 million acres of national forests are now managed with the purpose of utilization without loss of permanent value.

WORK OF THE UNITED STATES GEOLOGICAL SURVEY

"Classification of the public lands" during the last decade has developed into a leading branch of the work of the Geologi-

cal Survey. The field data accumulated as the result of three decades of geologic and topographic surveys, of stream measurement, and of detailed investigation of every resource now contribute to putting into practice this business policy. In practice land classification means simply the determination of highest use. To encourage development and at the same time to enforce wise utilization by preventing partial or wasteful use is to protect the public interest. With the different values of the land made known by adequate examination, the highest use can be determined and in so far as the statutes are in accord with economic law, the highest use can be assumed.

The scientific classification of the Nation's lands is now an integral part of the public land administration. The field work of the geologist and the engineer is made to contribute to a business policy in the management of the Nation's real estate along three distinct lines. Quantitative knowledge of the land and its resources is now made a preliminary; first, to disposition of lands under the various settlement and development laws; second, to reservation of lands from present acquisition pending the enactment of adequate legislation; and third, to valuation of lands where the statute provides for disposition at prices expressing known value. For each of these phases a statement of the past year's work will best serve the purpose of illustration.

The determination of the character and highest use of land for the purpose of securing its disposition under the appropriate law includes its classification as mineral or non-mineral and as irrigable or non-irrigable. Upon the questions of fact as to mineral character depends the passage of title from the Government under the agricultural or mineral laws and the applicability of certain railroad non-mineral land grants. The acreage classified for these purposes in the fiscal year ended June 30, 1912, was one and a half million acres. The questions involving water supply upon the public lands bear directly upon the administration of the statutes encouraging irrigation and dry farming, namely, the Carey Act, the desert land and enlarged-homestead laws, as well as various right-of-way statutes. Upon the determination by field engineers of the quantity of water

actually available for utilization in reclaiming the arid lands must wait the development of the remnant of agricultural lands in the public domain. Hydrographic classification of lands to serve this practical end aggregated last year more than two million acres.

The second phase of activity in land classification is one that provides for future rather than present disposition of the public domain. The Withdrawal Act of June 25, 1910, looks forward to better utilization in the future and opens up the question of amendment of present laws by specific provision for reservation from immediate disposal of oil and gas and phosphate lands and of power and reservoir sites. Under the authority of the statute, the Geological Survey recommended, last year, for executive withdrawal, more than one and one-third million acres of oil reserves, and almost one and one-fifth million acres of phosphate reserves, based on geologic data, and more than one-third million acres of water-power sites, and sixty thousand acres of irrigation-reservoir sites, based upon hydrographic and topographic surveys, and eighty-six thousand acres of public water reserves essential to the control of public grazing lands. The areas of the outstanding withdrawals are approximately four and three-fourths million acres of public lands chiefly valuable for oil and gas, three and one-third million acres of phosphate lands, more than one and four-fifths million acres of lands essential to water-power development, nearly one hundred thousand acres primarily valuable for irrigation storage, and eighty-six thousand acres of lands including springs or other watering places, unrestricted access to which by the public is essential in connection with the free use of the public range. The acreages thus described as withdrawn, however, include tracts of privately owned land, which are in reality unaffected by the orders of withdrawal although located in the larger legal subdivisions enumerated in those orders.

The third and most direct application of science to national stewardship is the valuation of the public coal lands. The coal-land law of 1873 is essentially a sales rather than a settlement law and provides for a minimum selling price. Since 1907 coal lands have been sold at appraised prices fixed by the Geo-

logical Survey on the basis of geologic field examination and chemical and physical analysis, valuation data of the latter kind being obtained from the Bureau of Mines, which is charged by its organic law with the analyzing and testing of coals and lignites.

Detailed classification of areas of the public domain into coal and non-coal land necessarily precedes valuation, and itself results in the annual restoration to full entry under the agricultural laws of ten millions of acres, while several million acres are annually appraised at their coal value. The total coal appraisement to August 1, 1912, has been sixteen million acres with a value of over seven hundred million dollars, which amount is nearly four hundred and fifty millions of dollars in excess of the minimum prices allowed by law. Yet the outstanding withdrawals of unclassified coal lands include sixty-eight million acres of which approximately seventy-five per cent is believed to remain in public ownership.

VALUATION OF COAL LAND

This practical application of refined geological and chemical science finds expression on so large a scale in the Nation's coal-land business that a brief resumé of the valuation basis is appropriate. Accessibility to transportation lines, position and number of coal beds, and quantity and quality of available coal, are the factors which enter into the determination of value.

The actual value of an acre of coal land is determined by multiplying the estimated recoverable tonnage by a value in cents per ton based on actual royalties, with allowances for interest, taxes, and uncertainties of tonnage. Starting with an assumed recovery of 1,000 tons per acre-foot for a solid single bed less than 500 feet deep, there is taken into account every factor affecting the possible recovery of its cost, such as depth, thickness, dip or pitch, partings, poor roof or floor, nearness of other beds, faulting or igneous intrusions. The price per ton is derived from the B. T. U. value of the coal obtained from air-dried, unweathered samples, cut in a definite way, as modified by ash, sulphur, proportion of fixed carbon,

by the physical properties of coking, stocking, etc., and its being suitable for any special use. The price may range from 3 cents a ton for a single bed of the highest-grade coking bituminous or anthracite coal of 15,000 B. T. U., down to 1-2 cent a ton for a single bed of sub-bituminous coal of 9,500 B. T. U., or less, or to as low as 1-40 cent for beds in areas containing better beds that will be worked first.

THE PRESENT POLICY

The land classification that began with a qualitative survey of the national domain is now rapidly tending to become a quantitative determination of every natural resource that gives value to these public lands. With exact information at hand as to relative worth and possible utilization of the public lands, it is possible both to administer properly the land laws of today and to plan more adequate legislation for tomorrow.

Abstract of paper presented before Eighth International Congress of Applied Chemistry. New York, Sept. 9, 1912

STATE WORK IN FOREST CONSERVATION
(*Eastern States*)

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This paper discusses what the eastern states are doing to develop their forests and to bring about a conservative use and maintenance of this natural resource. The eastern states considered are the New England States, New York, New Jersey, Pennsylvania and Maryland. These states contain an estimated area of 50 million acres of forest and woodland, 9 per cent of the total forest area of the United States. Under non-conservative cutting and unrestricted damage by fires the forest has deteriorated and there are thousands of acres of waste land requiring forest planting. These facts have come to be recognized within the past thirty years and within a little more than a decade a state forest policy has been developed in each of the states. This policy has included a state organization for the control and prevention of forest fires; state ownership and management of forests for demonstration of the practice of forestry, for protection of mountain watersheds and for recreation purposes; investigation and experiments in forestry to secure accurate data on forest growth and the results of silvicultural systems of management; assistance of the private owner in the practice of forestry; school, college and public education in forest conservation.

Fire protection problems have received greatest attention in each state because fire is the source of greatest waste. A well organized state and local force has been created and the emphasis in recent years placed upon measures of prevention such as patrolling, trail building, telephone construction and

the establishment of lookout stations; causes of fires are studied and means are being taken to eliminate them. Present systems of protection are well conducted but carelessness of the public is the root of the evil and requires further development of public sentiment by more strict enforcement of the laws and by means of education. Excepting in Maine and Rhode Island state forests have been acquired in each state. Such forests have great value for the demonstration of forestry practice, for protection of water supply and for recreation purposes. New York's constitutional amendment prohibiting cutting in the State Preserves precludes the practice of forestry. Other states are carrying out this practice on state forests to the advantage of the locality and the state in forest conservation.

The development of effective fire protection has hindered the states in experimental work and investigation and study of forest growth. Despite this a considerable number of such investigations have added materially to the fund of silvicultural knowledge and definite series of experiments have been started in several states. Nearly all the states assist owners by examining lands and preparing plans for forest planting and forest management. Such work has been limited by lack of time and sufficient force in the State Forester's office. Public interest in this assistance is increasing and a fair proportion of the advice thus given is used. Forest planting has received a great impetus by state assistance through distribution of suitable plant material at cost.

The agricultural colleges in all the eastern states give instruction in forestry and further public education is furnished through addresses, exhibits at fairs and elsewhere and by State Forestry Association meetings. There has been a wide distribution of publications on forestry consisting chiefly of State Forester's reports and bulletins as well as published proceedings of State Forestry Associations.

CONSERVATION AS APPLIED TO BITUMINOUS COAL INDUSTRY

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In connection with the discussion on Conservation of National Resources the coal industry will no doubt occupy an important place and to this end I will briefly recount a few of the conditions that confront the bituminous coal industry of the United States which will give at least some suggestions for discussion.

The question of conservation of the National Resources is a very laudable subject and one of great interest not only to scientists but to the entire present and future population of the United States. It is such a broad question that one could not hope to touch the great ramifications of this subject in a short paper, but as to its application to coal, suffice it to say that there are several conditions that confront the coal operator of to-day that were not even dreamed of a few years past. I would state first of all, that the general opinion of the people is that there is so much coal that little, if any, attention need be given to the conservation of it. This is especially true of the past history of the coal mining, for it is only within the last few years when the question of conservation of timber and National Resources became uppermost in the minds of some of the government officials, and through their efforts the public were brought to realize the condition which confronted them, on account of the waste of the fuel resources of the country. This condition of affairs would otherwise probably have gone on unheeded for many years had not these government officials brought it to the attention of the public for the reason that any statement made by those engaged in the producing of coal would likely have been received by the people as an attempt to boom the prices of their product and would not have received serious consideration.

This pioneer work of conservation has been so well done that almost every person to-day has been brought to consider in some way or other the question of conservation of the National Resources.

In order to get a clear idea of what we are about to discuss we should call attention to the location and general distribution of coals in the United States. This is very hard to do in a brief paper, as there are now some twenty-nine or thirty of the states of the Union that are known to contain large quantities of bituminous fuel, either in the form of lignite or true coal. The Eastern and most prolific of these coal fields are located largely along the Appalachian Chain of mountains consisting of the coal beds of Pennsylvania, Maryland, West Virginia, Virginia, Tennessee, Kentucky, Georgia and Alabama. The Central District comprising Ohio, Indiana, Illinois, Iowa, Kansas and Missouri, and the Western Coals, which are more or less lignitic in character, in the Rocky Mountain group, together with the coals in the north-west in Washington are likely the sources from which the coal supply of this country is to be secured. In Canada the main sources of supply are from the east, Nova Scotia and New Brunswick; on the west, Alberta, British Columbia and the Vancouver Districts. These with some coals in Mexico constitute practically the districts from which the coal supply of the North American continent are and will be supplied. From this statement it is readily discernable why the general public of the United States believe the coal is practically inexhaustible, and the apathy toward its conservation.

For this paper we will confine ourselves to a brief discussion of a few of the conditions that exist in the Appalachian Section, which will be more or less applicable to all the other districts, which refer very largely to conservation, and for other conditions affecting the industry would respectfully refer to the addresses of Mr. A. J. Moorshead of St. Louis, Mo. and Dr. James Douglass of New York delivered before the Chicago Convention of the American Mining Congress October 24-28, 1911. In many parts of this district mines have in the past been opened up very cheaply on account of their being drift mines requiring very little expense to open up and begin the shipping of coal pro-

viding of course that railroad connections were available for this purpose. As a natural consequence of the above, the coal production has always, except in a very few instances, been equal to and slightly in excess of the consumption and this condition can easily continue for some years to come. This very condition although to some advantage to the consumers for the time being is working a great injury to posterity along the line of conservation. In the early days of mining in the Pittsburgh District for instance only a very small portion of the entire bed was mined and shipped, over one-half probably close to 60% of the great Pittsburgh Coal Seam was left in the ground as only the best portion of it could be sold at a profit. This condition has continued although somewhat abated, up to the present time and probably to-day in this district there is not much in excess of 50% of the coal of this great seam recovered. The lost portion of the coal, which is of a poorer quality, containing many laminations of slate and other impurities; owing to fierce competition, and the strict specifications upon which coal is now being sold, renders it impossible on the part of the coal operator to produce this portion of the coal at a cost which would equal a price at which he can sell it. Consequently the commercial demands are preventing this great amount of the coal resources of this district from being conserved for future generations. While this loss is probably more in this great seam than in many others, yet a great amount of loss is also taking place in practically every Bituminous Coal seam now being worked.

The question naturally arises why does the Government permit this to exist? It is much harder to give an intelligent answer to this question than it is to propound it. First of all the laws of our country are not such that will permit the National Government to take cognizance of the matters which they have already relegated to state control. There are also national laws which prevent any combination of producers of coal that will in any way effect a cure for this trouble, on account of such a combination being in restriction of trade. Again the states will not individually take hold of this because of the fact that if one state should do this, the business of that state would be reduced to the advantage of some other state, which is a competitor in the

business, which would refuse to take such action as would restrict competition in any way. Again labor conditions are such that to produce these cheaper grades of coal requires a much larger expenditure of time and consequently costs more, and as stated above the selling price of this inferior quality of coal with the considerable amount of extra work necessary to produce a coal that would be marketable is not sufficient to meet the cost of production as the consumer would not be willing to buy this coal without he would get it for a much less price than he could buy the higher grade of coal. The natural or only result of these conditions is that this coal must be left in the mine. It has been stated by government officials, and I believe correctly, that during the past year in the mining of practically five hundred million tons of coal in the United States two hundred fifty million tons of coal were lost and in the losing of this coal it is not like some other commodity for instance a low grade of iron ore or ore containing precious metals that can be worked over again, it is irretrievably lost and cannot be recovered in the future. Consequently it seems to me that there is no phase of natural conservation to-day that calls for broader or deeper thought than that pertaining to the coal resources of this country.

If any person interested would take the time to investigate the cost of producing coal and the price at which it is sold they will very readily understand why the above condition continues to exist but there are several remedies that may be applied to this condition of affairs. First there might be devised some plan by the national government by which they could have general control of the mining situation. I am not prepared at this time to suggest just how this could be done. There have been a number of suggestions but they have been looked upon with considerable incredulity by reason of the fact that they have been brought forward and promulgated by coal operators or at least those interested in coal mines or properties and as stated above they do not have the same effect upon legislators for the reason that they believe that underneath their suggestions is a selfish motive and consequently little attention is paid to their suggestions. Another remedy it seems to me which is probably only a part of the first is that the government through some sort of a

commission should modify the resultant action of the present national law known as the Sherman Anti-Trust Law, so as to permit combinations, and by this I mean a combination that will in the end work out for the welfare of the whole community in that it will restrict or reduce the production of coal to the amount necessary to be consumed, and that it will permit, in selling of this coal, the obtaining of a price that will give to the men that labor at the mine a fair compensation for their work, together with all the safety obtainable; to the parties who have their money invested in the enterprise a fair return on their money, together with a sinking fund sufficient to pay back to them the investment which they have made in the mine by the time it is exhausted, and third guarantee to the consumer that he will not be overcharged for the fuel which he requires. This, while seemingly very easy is in reality very difficult to obtain and will require a great deal of thought and time to the working out of these conditions successfully. But as matters stand to-day operators are fearful of undertaking any such a proposition lest they be hailed into Court for acting against the spirit, if not the intent, of the Sherman Anti-Trust Law. If some such a commission were appointed, with power to act so that they were permitted to work out a regulation of the coal business which is so important not only to the present generation but also to future generations, I believe the first step would be taken toward the true conservation of the fuel resources of our country.

Another feature of the coal business which will be interesting to this congress is the subject of specifications for the purchase of coal. A great many of the larger consumers of coal to-day including the National Government have prepared specifications, and only upon which they will purchase their fuel, that are so rigid that it necessitates the loss of practically 50% of all the coal in the vein in order to produce the grade that they require. This will at once impress you, especially so far as the National Government is concerned, as being inconsistent, inasmuch as one branch of the government is crying for conservation while another is following a practise whose tendencies are diametrically opposite and the result of which in actual practise is a great waste of natural resources. Some of these specifica-

tions, while they appeal to the purchaser from a scientific standpoint as well as a commercial standpoint in the operation of his boiler and power plants, are ridiculous when they are applied to the actual operation of a mine. By way of explanation, I wish to state that in discussing this subject with a large purchaser of coal, who was determined to purchase on the B. T. U. basis, knowing nothing whatever of the operation of a mine, he suggested that the coal operator could pay the miners on the B. T. U. basis. To any person having any knowledge whatever of mine labor or the general conditions under which mines are operated this thought is too ridiculous to be given any consideration as coming from a normal mind and yet in the actual working out of some specifications for the purchase of coal this is practically what is being said to the coal operator in many places to-day.

I do not wish to be understood as condemning scientific progress in any way, but I am of the opinion that great advantage can be had in the way of conservation and equity between the purchaser and the producer of coal by having specifications which can reasonably be carried out without loss to the producer or requiring so much higher price for coal from the consumer who purchases coal on this supposedly scientific basis. This can be done by reducing the ash in the coal by special preparation at the mine, but no amount of desire on the part of either producer or purchaser can change the chemical composition of the coal, the ash constituent being practically the only one the producer can change and this generally at a considerable extra cost, but some of this can be taken out at the mine very readily and to give a premium for this or to demand a reduction in case it is permitted to go into the coal, I think would be entirely fair, but to ask a coal producer to furnish coal containing a certain chemical constituent which is something over which he has no control whatever is ridiculous from my point of view. This proposition of taking care of the ash at the mine brings up another line of conservation which must not be overlooked entirely. That is in order to get a large portion of these slates and ash producing constituents removed from the coal it is necessary to resort to washing. This requires a large amount of water and considera-

ble expense as well also an area over which the tailings from the washery can be gathered and concentrated so as to prevent their admission into and the pollution of the streams, for, as is well known, many states have already passed stringent laws regarding the pollution of the streams, which if the washings from the mines were permitted to enter would again subject the operator to severe penalties from the states. All of these conditions and requirements must in the end increase the cost of the coal to the consumer. I believe, however, that a great deal can be accomplished along the line of conservation in the way of taking out these objectionable materials without fastening such a heavy burden on the producer of coal as will prevent him from carrying them into effect.

There are so many of the above conditions coming up to the operators of mines to-day that it is producing a condition of great importance to the public and one I think that is to-day being overlooked very largely but should require careful consideration that is that those several requirements are putting out of the business to-day many of the small coal operators, and the tendency through legislation and various other conditions in vogue, are tending to permit only companies with a large amount of capital to remain in the business of producing coal and thus forcing out of existence the smaller or weak operators from the fact that they scarcely can compete in the markets as it stands to-day. I believe this tendency will increase until this great concentration or monopoly of business shall become such that reasonable regulations regarding the production and conservation of coal will be taken up by the National Government and handled upon intelligent lines instead of drastic measures gotten up for the purpose of cribbing certain interests as they seem now to be generally promulgated.

In conclusion will say that there are many other things in relation to the coal business which might be brought to your attention but as conservation will be the theme of your chief consideration, I believe that true conservation, which we all so much hope for, must come through and by a conscientious, intelligent, and fair method, which shall be formed on such broad lines as will, while conserving the resources for future genera-

tions, deal fairly and equitably with those engaged in the struggle for existance, commercially and morally, as well as physically, and any plan which does not include fair and equitable treatment in all of these phases and to all parties in interest must fail.

(*Abstract*)

FIRE LOSSES IN THE UNITED STATES AND THEIR PREVENTION

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Fire prevention as distinguished from fire protection or suppression, is a question of social economy coupled with sound architectural construction. It involves no chemical problems as does fire fighting.

Fire prevention concerns the removal of the causes of fires and the adoption of means for their suppression.

In 1907 the fire losses or those due to the actual destruction of property by fire amounted to \$215,084,709, or a per capita loss for the United States of \$2.51. Compare this with 33 cents, the average per capita fire loss in the leading European countries. Or making the comparison by cities of the same size, we find in Paris, France, a per capita loss of 47 cents as compared with Chicago, Ill., \$1.43; or Frankfort, Germany, 31 cents as compared with Cincinnati, Ohio, \$5.70; and Sheffield, England, 18 cents compared with Cleveland, Ohio, \$1.12.

Adding now to the total annual fire losses those wastes resulting from excessive expenditures obligated by fire protection on account of the greater fire hazard in the United States, we find that there was paid out in American cities in 1907 for additional public water supplies for fire fighting purposes over and above the supply needed for domestic consumption alone, the sum of \$28,856,235; for premiums on insurance, in excess of the amounts returned to the insured in the form of losses paid \$145,602,362; for fire fighting departments \$48,940,845, and for miscellaneous items including private fire protection, a total sum, which added to the annual fire losses aggregated \$456,486,151. Taking one item alone of fire waste, namely, maintenance of fire depart-

ments, we find that in Europe the average annual cost amounts to 20 cents per capita, in America \$1.53 per capita.

Added to this story of property waste is that of loss of life. In 1907 there were killed by fires in the United States 1,449 persons and there were injured 5,654 persons.

It is a worn out fallacy which assumes that the fire loss is borne by the insurance companies. They bear no loss, but act merely as collectors and disbursers. The losses are a tax on every man. For an example, take cloth. It is insured in transportation, in the warehouse, in the factory, in the drygoods establishment, and in the tailor's shop. Each one of you who buys cloth pays this tax.

Beyond the individual pecuniary interest in his own losses from fire, there is also the obligation of each citizen to his fellows, to protect his own property and so conduct his own affairs as not to endanger the lives and property of his neighbors.

The average citizen indiscriminately sympathizes with his neighbor whose property has been destroyed, whereas often he should give only his condemnation. Only too often is the neighbor the sufferer from the carelessness or parsimony of those who surround him with fire traps. There have been enacted in some cities reasonable building codes, which should, if properly enforced, go a long way toward the reduction hereafter of the number and character of inflammable buildings. Measures should be taken to study the fire hazards in each city in relation to the topography and the accessibility for fire fighting purposes. Based on such a survey it should be possible to restrict conflagrations by directing fire resistant construction along such lines as would divide the city into protected areas by fire proof walls of modern construction.

The masonry building is not a fire stop, however, unless each window is framed with metal and protected with wire glass. Having confined the conflagration to districts of the city, consider the individual building. The risk may be lessened especially for residences by the abolition of wooden shingles, which may come about in the course of new structures or repairs to a certain percentage of old roof. Ultimately as the inflammable buildings disappear and are replaced by those of better con-

struction, the whole city may be rendered as relatively fire resistant as are European cities.

As an example, fifteen years ago one-third of the total fire loss in New England was on factory buildings. The New England factory insurance inspectors have in the interval so reduced that loss by preventive measures, that in the last fifteen years, only eight fires exceeding \$100,000 loss have occurred on one and one-half billion dollars of insured property. And today fireproof factory construction is as cheap as 10 to 15 cents per cubic foot, while inflammable residence construction rarely costs less than 20 cents.

Finally take home with you the memory that one cause for these fires is your personal feeling that there is no reason why a fire should happen to you. All fires are of the same size at the start. The first five minutes of a fire is the period that determines whether it shall be promptly extinguished or blaze into a conflagration. Are you prepared to fight a small fire by any means whatever? Every fire is the personal responsibility of the occupant of the building for the first five minutes of its life.

THE ACTIVITIES OF ENGLAND, WALES AND THE DOMINION OF CANADA IN BEHALF OF THE CONSERVATION OF NATIONAL RESOURCES

(NOTE: The information contained in this paper has been secured through the good offices of His Excellency, James Bryce, Ambassador of the British Empire to the United States.)

ENGLAND AND WALES

Waters

The government's activities in water conservation have been directed toward the following purposes:

- (a) To secure, maintain and protect adequate supplies for domestic and municipal needs, and for the irrigation of crops;
- (b) To secure the fullest development of water powers, with a view to maximum benefits to the Community and to the state or national government;
 - (1) through governmental inquiries and investigations;
 - (2) through legislative requirement;
 - (3) through administrative governmental regulations; and
 - (4) by general organised agreement (through national or state societies or similar organisations) in behalf of a practical conservation of natural resources.
- a. (1) The provision of adequate supplies of water for domestic and municipal needs and the prevention of water pollution have been the subjects of very important governmental investigations in England and Wales during the last fifty years.

These investigations have mainly been carried out by various Royal Commissions who have reported on them in much detail.

A Royal Commission, appointed in 1866 to inquire as to the supply of unpolluted and wholesome water available in England

and Wales, and as to the existing water supply of the Metropolis, issued a voluminous report on these subjects in 1869.

At the same time the state of sanitation generally throughout the country was being investigated by the Royal Sanitary Commission of 1869, who dealt with the question of water supply in one of their reports, whilst another Royal Commission appointed in 1868 to deal with the question of the pollution of rivers made a comprehensive report in 1874 on the domestic water supply of Great Britain.

In 1879 a Parliamentary return was prepared and issued by the Local Government Board giving particulars of the supplies of drinkable water in every urban sanitary district in England and Wales and in 1888 a similar return was published giving much information respecting the water undertakings in the largest towns in the United Kingdom. The Water supply of London has also been specifically inquired into and reported upon by several Royal Commissions and Parliamentary Committees, their labours resulting in 1902 in legislation creating a special Water Board for the Metropolis in lieu of the eight Water Companies which up to that time had provided the necessary supplies of water.

Some Royal Commissions on subjects concerned with water, rivers, etc., have made recommendations on the question of water, notably the Royal Commission on Sewage Disposal (which has not yet completed its labours), the Royal Commission on Salmon Fisheries and the Royal Commission on Canals and Waterways.

In their recommendations the Commissioners have generally advocated the creation of an adequately equipped Central Government Authority and the formation of Local Boards to deal exclusively with all questions relating to water. During the year 1910 a Joint Select Committee of both Houses of Parliament appointed to consider a Bill for the protection of water supplies reported to Parliament strongly advocating the measures recommended by these Commissioners and in the same year a return was ordered by the House of Commons showing as regards every water undertaking in England and Wales:—

- (a) the powers, if any, under which the undertakers are authorised to supply water;
- (b) the limits within which the undertakers are authorised to supply water;
- (c) the places actually supplied;
- (d) the sources of the supply, their nature and sufficiency;
- (e) particulars as to the works, the quantity and quality of the water supplied;

and also, as regards every district in England and Wales:—

- (a) the area and population of the district, and the number of houses therein;
- (b) the number of houses supplied with water from a piped service;
- (c) the names of the undertakers providing a supply of water;
- (d) the source, nature and sufficiency of the supply where there is no piped service.

The information required for the preparation of this return is being collected and summarised by the Local Government Board, the Department of Government concerned with water from the point of view of the public health.

Other Government Departments are concerned with questions relating to water namely the Board of Agriculture and Fisheries and the Board of Trade.

In addition to the formal investigations made specifically by Royal Commissions, numerous scientific inquiries have been made by expert officers, for the Local Government Board, as to the contamination of water supplies, in connection with outbreaks of infectious disease, the dangers of lead poisoning by waters possessing plumbo-solvent properties, etc.

The Board take every opportunity of impressing Local Sanitary Authorities with the necessity of safeguarding their supplies of water. The published memoirs on underground water supplies, in various counties in England and Wales prepared by officers of His Majesty's Geological Survey should also be mentioned.

(2) The law on the subject of water is to be found in several general Acts of Parliament, in numerous local and private Acts and in the Acts confirming Provisional Orders issued by the

Board of Trade and the Local Government Board as well as in many decisions given in Courts of Law.

A very complete compendium of the law is contained in the treatise by Michael and Will "On the law relating to gas and water." Butterworth & Co.

The following are the principal general Acts affecting the question of water:—

the Waterworks Clauses Acts, 1847 and 1863,
the Gas and Water Facilities Act, 1870,
the Public Health Act, 1875,
the Rivers Pollution Prevention Acts, 1876 and 1893,
the Public Health (Water) Act, 1878,
the Water Rate Definition Act, 1885,
the Water Companies (Regulation of Powers) Act, 1887,
and the Public Health (Water Supplies Facilities) Act, 1897.

As regards pollution of rivers mention may also be made of the legislation affecting particular rivers namely, the Mersey and Irwell Joint Committee Act, 1892, the West Riding of Yorkshire Rivers Act, 1894, and the Rivers Pollution Prevention (Border Councils) Act, 1898.

In rural districts it is the duty of the Local Sanitary Authority under the Public Health (Water) Act, 1878 (regard being had to the provisions of the Act) to see that every occupied dwelling-house has within a reasonable distance an available supply of wholesome water sufficient for all domestic purposes. It is also enacted that (in a rural district) a new house must not be occupied until a certificate has been issued by the Local Sanitary Authority stating that there is within a reasonable distance a sufficient supply of wholesome water.

The Local Sanitary Authorities are also empowered to secure the closure of all polluted wells, tanks, or cisterns.

Where Local Authorities, Companies or individuals require statutory or official authority for purposes connected with water supply, their powers, rights and duties are duly defined by local Acts of Parliament but the control of water sometimes remains in the hands of private proprietors without any Parliamentary powers or restrictions.

(3) Circulars have been issued from time to time by the Local

Government Board reminding the Local Sanitary Authorities of their responsibilities under the Public Health Acts for securing the provision of proper and sufficient supplies of water and urging them to take all practicable steps to improve and protect supplies obtained from various sources.

The Board have also issue for adoption by Local Authorities and Water Companies possessing the requisite statutory powers a model code of byelaws for preventing the waste, undue consumption, misuse or contamination of the water they supply.

The Board also examine and report to Parliament on the provisions affecting water in all Bills for local Acts with a view to securing that any necessary amendments shall be made in them.

(4) The question of conservation of water supplies with a view to securing the maximum benefit to the community and the State has been pressed with increasing persistence on the Government by the Royal Commissions on Sewage Disposal, on Salmon Fisheries, and on Canals and Waterways as well as by the Parliamentary Committee on the Protection of Water Supplies, and by several societies such as the County Councils Association, the Royal Sanitary Institute, the British Association of Waterworks Engineers and the Underground Water Preservation Association.

Lands

(a) Except in the case of sand dunes the area of land in Great Britain requiring special treatment merely to prevent surface erosion is negligible, and nothing has been done in any systematic way to prevent such erosion.

In the case of sand dunes steps have been taken in one or two instances to afforest them and in others they have been planted with such grasses as the Seamarra (Psamma arenaria) and Lyme grass (*Elymus arenarius*).

(b) In Great Britain the value of rotations is well understood and all cultivated land is cropped according to definite systems which are specially adapted to suit the condition of soil, climate markets, &c., in the districts where each is used. Furthermore as is necessarily the case in a country where much of the land has

been under cultivation for hundreds of years one of the first considerations a farmer keeps in mind is the necessity of maintaining the fertility of the land not only by means of suitable rotations but also by the careful conservation and use of manure produced on the farm and by the purchase of artificial manures and concentrated feeding stuffs.

In the majority of cases, the practices in vogue cannot be attributed directly to either Government encouragement or to the action of organised societies but are the outcome of the accumulated experience of generations of farmers. In part, however, these practices are based on the results of scientific investigations carried out in comparatively recent times—as for example the Rothamsted researches—and in part they are due to the efforts of such bodies as the Royal Agricultural Society of England and the Highland and Agricultural Society of Scotland in disseminating agricultural information, encouraging the adoption of improved methods, and in initiating and encouraging original research. Much educational and research work is now being carried on by State-aided Universities and Colleges under the supervision of the Board of Agriculture. The various Agricultural Holdings Act which brought into definite form principles which previously were generally though not universally recognised, have done much to promote good farming and to conserve the natural resources and fertility of the land.

In explanation of the effects of these Acts it may be pointed out that the greater part of the agricultural land in this country is cultivated by tenant farmers who hold farms under a yearly tenancy or (particularly in Scotland) on a lease for some stated period—often nineteen years.

The general principles established by law and underlying all recognised customs (which unless they contravene an Act of Parliament are legally binding on both landlord and tenant, in the absence of any special agreement) are that

(1) A tenant must cultivate his farm in such a way as to maintain its fertility, failing which the landlord can claim compensation for the deterioration caused and

(2) He is encouraged to improve and make the most of his farm by being given the right on leaving it to claim compensa-

tion for the unexhausted value of any improvement he may have made.

The essential provision of the various Acts may be summarised as follows—Where a tenant has made on his holding any improvement, he shall be entitled at the determination of the tenancy, on quitting his holding, to obtain from the landlord, as compensation for the improvement, such sum as fairly represents its value to an incoming tenant. The improvements to which this applies are specified in a schedule which includes all that would be carried out under ordinary circumstances.

With regard to rotation of crops, very often and in fact almost always, in old agreements between the landlord and the tenant there was a clause which bound the latter to follow a certain rotation usually the one common in the district—and which prevented him selling off the farm certain crops, with a view to maintaining the fertility of the farm. These crops which had to be consumed on the farm by stock were generally straw, hay and turnips so that the lease or agreement practically determined the amount of dung made on the farm each year.

Under the Agricultural Holdings Act of 1906 a tenant is given full freedom as to cropping and disposal of produce (except that he must conform to the agreement in the last year of his tenancy): “Provided that he . . . shall make suitable and adequate provision to protect the holding from injury or deterioration, which provision shall, in the case of disposal of the produce . . . consist in the return to the holding of the full equivalent manurial value of all crops sold off or removed in contravention of the custom, contract or agreement.” If the tenant exercises the right thus given in such a way as to injure the holding the landlord can, not only obtain compensation for the damage done, but also obtain an injunction restraining the tenant in the exercise of such right.

The most important Agricultural Holdings Acts were passed in 1883, 1900 and 1906 respectively. In 1908 all three were consolidated in one Act. Copies are enclosed.

Forests

There are less than 70,000 acres of Crown Forests in Great Britain, and private woods, constituting roughly 97% of the whole wooded area, are under no restrictions as to sylvicultural management.

(a) Nothing is done directly by the State to preserve forests against wasteful cutting. There is a general feeling among land-owners that woods which are cut over should be replanted, and this is very generally done. It is hoped that the technical advice which the Board of Agriculture are about to provide for land-owners in England and Wales will stimulate interest in sylviculture and lead to improved methods of utilisation.

Damage from fire is seldom of a very serious character. The Railway Fires Act 1905 (of which a copy is enclosed) makes Railway Companies liable for fires resulting from locomotives to the extent of £100.

(b) Apart from the planting which is continually going on in State Forests and private woods an extension of forest should take place under the operations of the Development and Road Improvement Funds Act, 1909.

The Development and Road Improvement Funds Act of 1909, above cited, appears to be an effective measure of conservation. It provides among other things for the establishment of a "development fund" into which shall be paid (1) such moneys as may from time to time be provided by Parliament, (2) any sums received by the Treasury by way of interest on or repayment of loans made under the Act, and any profits or proceeds derived from the expenditure of any moneys which by the terms on which the advance was made are to be paid to the Treasury, and, (3) there is appropriated out of the "Consolidated Fund" or the growing produce thereof, the sum of five hundred thousand pounds per year, beginning the thirty-first day of March, 1911. It is also provided that the Treasury may accept gifts to be devoted to the objects and purposes of the Act.

The "development fund" may upon the recommendation of the Development Commissioners, who are appointed by His Majesty, make advances to a Government department, or

through said department to any public authority, university, college, school, or institution, or an association of persons or company not trading for profit. Such advance may either be made as a grant or a loan, and upon such terms and subject to such conditions as the Commission may think fit for any of the following purposes.

(a) Aiding and developing agriculture and rural industries by promoting scientific research, instruction and experiments in the science, methods and practice of agriculture (including the provision of farm-institutes), the organization of co-operation, instruction in marketing produce, and the extension of the provision of small holdings; and by the adoption of any other means which appear calculated to develop agriculture and rural industries;

(b) Forestry (including (1) the conducting of inquiries, experiments, and research for the purpose of promoting forestry and the teaching of methods of afforestation; (2) the purchase and planting of land found after inquiry to be suitable for afforestation);

(c) The reclamation and drainage of land;

(d) The general improvement of rural transport (including the making of light railways but not including the construction or improvement of roads);

(e) The construction and improvement of harbours;

(f) The construction and improvement of inland navigations;

(g) The development and improvement of fisheries; and for any other purpose calculated to promote the economic development of the United Kingdom.

THE DOMINION OF CANADA

Lands

The Experimental Farms Branch of the Dominion Department of Agriculture may scarcely be said to be doing anything in behalf of a practical conservation of national resources along the lines of maintaining or improving soil fertility through a

rotation of crops, by improved culture or by the application of fertilizing materials either (1) through governmental inquiries and investigations, (2) through legislative requirement, (3) through administrative governmental regulations, or (4) by general organized effort (through national or state societies or similar organizations)—unless possibly experimental work in soil cultivation, crop rotation, and manuring; demonstration work in these same lines; and the diffusion of information so gained by means of reports, bulletins, articles in periodicals, and popular lectures might be said to in some measure come under the head "governmental inquiries and investigations."

Accepting this as a proper interpretation of the head "governmental inquiries and investigations," then during the past twenty-five years the work of the Dominion Experimental Farms has served to bring prominently, persistently and affectively to the attention of Canadian farmers the necessity for thorough and scientific cultivation, the value of short and what might be called nicely balanced rotations, and the imperative need for and proper use of fertilizers if crop-producing powers of soils are to be increased or even prevented from falling off.

Cultural Methods. Repeated experiments on the various Dominion Experimental Farms throughout Canada served to establish the value of (1) thorough cultivation, (2) timely performance of cultural operations, and (3) cultural methods suited to (a) different crops and (b) various soils. These facts once established, their wide diffusion by bulletin, report, newspaper article and institute address and the repeated carrying on of striking demonstration work along the lines mentioned, has served to bring them to the attention of practically every Canadian farmer. While all have not profited to the extent that might have been hoped, it is doubtless safe to say that all have been affected in a greater or less degree and many have been benefitted immensely through their accepting and putting into operation the teachings set forth as above indicated.

Crop Rotation. The necessity for proper crop rotations was not so early appreciated as the importance of good cultural methods, on the Dominion Experimental Farms, and so did not receive so much attention for some years. During the last

thirteen or fourteen years, however, fairly extensive experiments have served to demonstrate the exceedingly great importance of following suitable rotations in the various lines of farming, whether grain farming, mixed farming or purely live stock farming and whether in the eastern, central or western parts of the Dominion.

The value of the rotation having been proven, immediately steps were taken to spread the information. Reports and bulletins have been issued or are in press, articles have appeared in the agricultural or other newspapers and periodicals and very many addresses have been delivered on the subject in all parts of Canada. Demonstration work was begun on all the Farms in the Experimental Farm system and some thirty-five different rotations are now under way. This demonstration work is undoubtedly having a great effect on our farmers.

Fertilizers. Among the problems a study of which was begun at the very inception of the Experimental Farm system, the use and value of fertilizers of all kinds was considered as probably the most important it was attempted to solve.

The proper treatment or conservation of, and the most advantageous methods of utilization or application of barnyard manure were carefully investigated with the result that many of the practices or methods commonly followed in this country were found to be either wasteful or relatively unprofitable. Continued efforts to inform farmers as to the most economical methods of using this invaluable, readily available and easily applicable natural fertilizer are having the most beneficial effect, particularly in the eastern and extreme western as opposed to the prairie provinces. The effective diffusion and general putting into practice by the farmers of the information gained on this subject has been and will continue to be of incalculable value to the country.

A long continued and exhaustive study was made of the manurial value of crop residues. Among those investigated the residues from legumes proved to be of the greatest value. Many experiments have been conducted and are still being undertaken to secure data as to the exact manurial value of such crop residues. The information as gained on this subject (as on all others) has

been and continues to be so published as to ensure its most prompt and widest circulation.

The value to Canada of the wide dissemination and general use of the information gathered on the effects of a clover, alfalfa or, to a lesser degree, other leguminous crop upon the succeeding crop can scarcely be estimated.

What are commonly known as commercial fertilizers have been experimented with for twenty-five years; but so far these have for the most part failed to demonstrate their need in this country, with the possible exception of their value for orcharding purposes in the more freely watered portions of the Dominion.

In conclusion, it might be said that investigational work carried on at the various Experimental Farms in the system in connection with soil cultivation, crop rotation and fertilizer utilization has been rich in results in the way of data gathered, and most strikingly effective when such information was disseminated and when findings were properly demonstrated on the various Farms and elsewhere.

Forests

The forests of Canada formerly covered practically the whole of the land except the prairies of the western provinces. In southern Ontario there was a large area covered with hardwood trees such as black walnut, oak, chestnut, tulip tree, hickory, black cherry and buttonwood. Most of the land upon which this forest stood is now being turned into farms, and only a few small scattered areas of timber are left here and there.

Along the Laurentian ridge from the province of Nova Scotia westward to the Rocky Mountains there stretched a forest practically continuous of spruce, white and red pine, tamarack, cedar, jack pine, with some hard maple, yellow birch, oak, beech and ash. On the northern slope of the Laurentian ridge the species were reduced to spruce, jack pine, tamarack and poplar.

In the province of British Columbia practically the whole of the land was timbered with Douglas fir, cedar, spruce, western white pine, yellow pine and some other less important species, and practically no hardwoods.

Administration

The administration of the forest lands is divided between the provincial and the federal governments. The provinces of Nova Scotia, Prince Edward Island, New Brunswick, Quebec, Ontario and British Columbia administer their own forest lands, and the federal government administers the forests in the provinces of Manitoba, Saskatchewan and Alberta, in the Yukon district and the North West Territories.

Federal Administration

The forests under federal jurisdiction are administered through the Forestry Branch of the Department of the Interior, and naturally separate themselves into the following divisions:

Tree planting on the prairie farms. In 1900 arrangements were made for establishing a forest nursery so as to furnish a supply of trees for planting on prairie farms for shelter belts and wood lot purposes. The department gives instructions to the farmers as to the species to be planted, how the plantations should be arranged and how they should be cared for.

There is a staff of inspectors who have had training in nursery work and the care of trees attached to this division, who visit the farms of the applicants and assist them in laying out their plantations, in preparing their lands and in selecting the trees which they require. As the thorough cultivation of the land is an essential to successful tree planting on the prairies, this is made a special requirement before trees are sent out. The department furnishes the trees for planting free of charge, except in connection with coniferous species for which, on account of the cost of production and the difficulty of raising them in large quantities, a charge of \$1 per hundred is made.

Since the distribution of trees was begun, sixteen million trees have been distributed and planted on farms in the prairies, and of these fully 85 per cent have been entirely successful. The assistance thus given by the department has made it possible for the farmers to improve their home surroundings and has added very much to the beauty of the farms on the western prairies.

Exploration of the public domain. There are two reasons for making the exploration: one is to obtain the information as to the timber which is upon the Crown lands, and the other is to determine what lands are not suitable for agricultural purposes and should be set apart for permanent administration as timber lands.

For several years this work has been carried on steadily and as a consequence considerable information in regard to the timber is being accumulated. During the past year six survey parties, all of which were in charge of a trained forester, were making investigations of this kind. Unfortunately it has been found that although there are very large areas of land which are more or less timbered, the area of mature timber is but a small fraction of the whole. Repeated fires which have occurred in past years have evidently destroyed vast areas, and over the greater part of the northern forest the timber is so small in size that it is not yet of much use and will have to be carefully guarded for a period of years before it can be considered merchantable.

Forest Reserves. As a result of the examination of the public lands as above mentioned, 16 million acres have already been set apart by the Forest Reserves and Parks Act for forest purposes. These lands are withdrawn from settlement or from disposal in any other way than under the provisions of the Forest Reserves Act. The Forest Reserves Act provides that the timber may be disposed of under proper regulations and that leases for mining, water power and other purposes, consistent with the purposes for which the reserve is set apart, may be granted. Special provision is made for regulations for the protection of the timber from fire and trespass, the protection of the game, and for any other purposes that may be necessary to carry out the full intent of the Act.

These forest reserves are divided for administrative purposes, the divisions depending on location and accessibility. Some of the smaller scattered reserves throughout the prairie country are as small as one hundred square miles, while others are as large as three or four thousand square miles. On each of these reserves there is an officer in charge who is called a Forest Supervisor. The Supervisor is usually a technically trained man, but

is not necessarily always so as training, experience and administrative ability sometimes have pointed out a man as fit for this position without special training. There is also connected with each reserve a forest assistant who is always a man who has taken a full course in a forest school. He is the technical advisor to the Supervisor. There is also on each reserve a corps of forest rangers, each of whom has a portion of the reserve from one hundred to two hundred square miles in extent assigned to him which he is required to protect from fire and trespass, and in which he is to supervise all cutting operations that may be carried on and see that the regulations in regard thereto are observed.

The preliminary work which is being carried on on each reserve is to clear out all trails and roads so as to make all parts of the reserve easily accessible, which is particularly necessary to prevent fire; the locating of the forest rangers on their own districts within the reserve so that they may be immediately in touch with their work; the construction of telephone lines so that the supervisor may be able to keep himself informed as to the work which is being done by the forest rangers and may have early information of the occurrence of fires or of any matters where the forest rangers may require his assistance or advice.

Small buildings are being erected also at convenient places where a stock of tools may be kept that are likely to be required in case of fire.

The number of miles of roads and trails so far constructed is 144. No telephone lines have yet been constructed, but they are in the course of construction during the present year and it is expected that about 250 miles will be completed before the season closes.

The regulations in regard to the cutting of timber require that the trees to be cut should be marked by a forest officer. The timber on the reserves is not being withdrawn from use, but it is the intention that no cutting should be done except on well-defined plans which would provide for the reproduction of the forest. The forest assistant makes a careful study of any tract upon which the privilege of cutting is being allowed, marks the trees so as to leave provision for a supply of seed being secured by natural means, and arranges in what other way the cutting

should be supervised so as to produce the results aimed at. The person obtaining the privilege of cutting is required to pile the brush and debris resulting after the lumber operation. This is burned at a suitable season, or in some cases may be disposed of by scattering it so that it may lie flat on the ground. This is determined by the forest assistant as the circumstances may decide. This system is being carried out in connection with all new disposals of timber, but has not yet been extended to the operations of lumbermen to whom licenses were granted prior to the setting apart of the reserves.

The technical staff engaged in this work of forest reserve administration consists of fourteen men, the number of Supervisors is eight, and the number of rangers is eighteen. Checking and co-ordinating the work on the different reserves is carried out by district inspectors, of whom there are now three. These are men who have been technically trained as foresters, who have had some experience in forest administration and have shown special administrative ability.

Reforestation work on the Forest Reserves

On most of the forest reserves the question of natural reproduction of the forest and of artificial reforestation has been delayed until the protective system was thoroughly well organized. On all of the reserves of the prairie districts very small nurseries of forest trees in charge of the Forest Supervisors have been started, and experimental work in reforestation has been carried out. Only a few acres have, as yet, been planted, and these have been done mainly in an experimental way to determine what species would be best to plant and what methods of planting should be followed. This has now been determined, and arrangements are being made for the development of the nursery work as rapidly as possible. On the Spruce Woods Forest in Manitoba, which is one of the reserves where artificial reforestation would be especially required, a nursery is being established which will be capable, in time, of turning out one hundred thousand trees per year.

Fire Ranging

In the territory which has not yet been included in the forest reserves, and a considerable portion of it is still unsettled and practically uninhabited a patrol of fire rangers is kept at work. The number employed in this work for the past year was 129. These men patrol the line between the settlements and the timber lands, travelling along the roads and trails of the districts beyond settlement, posting up notices giving the provisions of the Fire Acts, warning people whom they meet of the danger of fire, and taking such steps as may be necessary to extinguish any fires that may occur. These fire rangers have done a great deal of good in preventing fires, but the number is small yet for the large districts which they have to cover, being in many cases hundreds of miles.

THE PROVINCE OF ONTARIO

Farm Planting. In connection with the Ontario Agricultural College at Guelph a lectureship in forestry was established and the lecturer was also given charge of establishing a nursery from which trees could be supplied to farmers for replanting denuded areas on their farms, which were not good agricultural lands. The number of trees distributed and planted on farms in Ontario from this nursery up to the end of 1910 was about two million. The Government has also done some replanting on sandy lands in the agricultural parts of the province which were still in Government ownership, or have been repurchased for that purpose. The area replanted, does not exceed ten thousand acres. The plantations have been generally successful.

Timber Explorations. Most of the forest land in the province of Ontario has been explored so that the Provincial authorities have a fairly good idea as to the quantity of timber which is still standing on Crown lands. The quantity of pine has been estimated by them at twenty billion feet, and the quantity of pulp-wood, mainly spruce, at two hundred and eighty million cords. Most of the northern forest has suffered severely from fire and the mature timber is found only in scattered areas.

Forest Reserves. The area set apart as forest reserves in the province of Ontario is 12,500,000 acres. Since these areas were reserved special patrols of fire rangers have been placed on them, but no staff of technically trained foresters has been appointed, nor has there been any attempt to improve the methods of administration, except in the respect of providing a somewhat more complete fire patrol than on areas outside of the forest reserves. The reserves include some very fine tracts of mature white pine.

Fire Ranging. The province of Ontario was the first administrative authority of the Dominion to establish a patrol of fire rangers, the first patrol having been established in 1885. The number of fire rangers so engaged in 1910 was 925. Their duties are chiefly to patrol the district of which they have charge, post fire notices giving warning to settlers and travellers, and extinguish fires when they occur.

THE PROVINCE OF QUEBEC

Farm Planting. No distribution of trees to farmers has yet been made by the province of Quebec, but a small nursery has been established which will be a demonstration tract for young men who are studying forestry, and from which nursery stock may be supplied to farmers and stock may be obtained for replanting some of the denuded areas of the agricultural districts.

A plantation has already been made on light sandy lands in the vicinity of Lachute under the supervision of the foresters in the employ of the Government.

Timber Exploration. The provincial government has made some exploration of the public domain to determine the timber which the province has, but this exploration has not been sufficient to give a definite idea of what timber there is available. Estimates have been made as to the timber in this province, but one of them can be wholly relied on as the information on which they are made is insufficient. The work has not been carried on in a systematic manner.

Forest Reserves. The Province of Quebec has a large forest reserve area amounting to 111,400,900 acres. This covers practically all of the non-agricultural land in the province of

Quebec. The organisation of the forest reserves has not been carried out very thoroughly. There is a small patrol of fire rangers, sixty-eight in number last year.

The technical staff consists of two men whom the Government had trained in the Yale Forest School and who also studied forestry in France. They are conducting a school in connection with the University of Laval for training men for their work. The staff is still very small for the area of forest reserve which has to be administered, and is not in a position to do more than to make studies of special matters that arise.

Fire patrol. A patrol of fire rangers is maintained in the forested districts, numbering in 1910 511 rangers.

PROVINCE OF NEW BRUNSWICK

Nothing has been done in the way of farm planting or the provision of nursery stock for such purposes by the Government. Most of the timber lands in the province have been fairly well explored so that the Government has a fair idea of the quantity of timber which is available.

No forest reserves have been established, as it has been considered that so much of the area of the province is non-agricultural land that what is necessary is to select the lands that are agricultural.

A patrol of fire rangers numbering 150 was carried out in 1910.

PROVINCE OF NOVA SCOTIA

In the province of Nova Scotia no provision has been made for farm planting or a forest supply of nursery stock.

In the matter of timber exploration the Government of the province arranged with Dr. B. E. Fernow, Dean of the Faculty of Forestry, University of Toronto, to make a survey of the timber of the province, and he has reported giving the following results as to the stand of saw timber in the province (mainland only):

| Type | Stand per acre Ft. B. M. | Area acres | Total Stand Ft. B. M. |
|-----------------------------------|-----------------------------|---------------|--------------------------|
| Virgin and semi-virgin | 12,000 | 94,496 | 1,133,952,000 |
| Moderately culled & 2nd growth | 3,000 | 1,318,964 | 3,956,892,000 |
| Severally culled & burned | 1,000 | 3,192,175 | 3,192,175,000 |
| Green barrens & old burns | 300 | 1,138,730 | 341,619,000 |
| Total stand of timber— | | | 8,624,638,000 |

As most of the forest lands in the province of Nova Scotia have been alienated in fee simple the Government has not established a system of fire patrol similar to that established in the other provinces. The law provides, however, that in each county a chief ranger shall be appointed who will have charge of the patrol work in that county and may put on such assistance to the patrol as may be necessary. The cost of the patrol is paid by assessment on the lands which are benefited. This system has worked out very satisfactorily. During 1910 thirteen chief rangers and a number of sub-rangers were employed in this service.

PROVINCE OF BRITISH COLUMBIA

The province of British Columbia is so largely a forest province that no provision has been made or is considered necessary for farm planting or to provide nursery stock therefor. For the same reason no forest reserves have yet been established.

The fire patrol system has been in existence for three years and in 1910 there were thirty-eight rangers appointed.

During the past session of the legislature a new forest Act was passed which provides for the establishing of a forestry division in the Department of Lands, which will have charge of the protection and administration of the forests of the province. Several foresters with technical training are being appointed and the intention is to thoroughly organize and develop the work of forest administration on advanced lines.

Minerals

The mineral rights in the provinces of Manitoba, Saskatchewan, Alberta, Northwest territories, Yukon and in the Railway Belt and Peace River Block in British Columbia, are disposed of by the Dominion Government but the actual mining operations in these provinces are controlled by the provincial governments. In the remaining provinces,—Nova Scotia, Prince Edward Island, New Brunswick, Quebec, Ontario and British Columbia, the mining rights and jurisdiction over the mines are vested in the provinces.

Provincial Acts relating to Conservation

The Provincial Acts make provision for the safety of the persons employed in the mines and also in a general way provide for the conservation of mineral resources.

Nova Scotia

In Nova Scotia provisions are made for the filing of the plans of all abandoned coal mines.

Ontario

The Province of Ontario has reduced the waste of natural gas to a minimum by making provisions¹ for the plugging of all abandoned oil or gas wells, and by levying a tax of two cents per thousand feet with a rebate of ninety per cent. when the gas is used in Canada.² The Mining Act of Ontario also provides for the filing of the plans of all abandoned metal mines.

British Columbia

Although many mines in Nova Scotia are equipped with mine rescue apparatus, British Columbia is the only province in the Dominion which requires such apparatus to be installed at the mines. The following are the provisions of the Coal Mines Regulation Act³ in so far as they relate to mine rescue work:—“There shall be established by the owner, agent, or manager of every colliery such number of oxygen helmets or some form of mine rescue apparatus as may be approved by the Minister of Mines. Such mine rescue apparatus shall be constantly main-

¹Statutes of Ontario, Chap. 47, 1907-

²Statutes of Ontario, Chap. 9, Part II., 1907.

³Coal Mines Regulation Act, 1911.

tained in an efficient and workable condition and shall in all cases be so stored or placed in or about the mine as to always be available for immediate use."

"The Lieutenant-Governor in Council may from time to time establish mine rescue stations for the purpose of supplementing, in case of need, the colliery installations and also for the purpose of training the holders of certificates of competency under this Act. It shall be incumbent on the owner, agent, or manager of every operating mine to have all certified officials who are physically fit, and not less than three per cent. of such number as the Chief Inspector of Mines may deem sufficient of the workmen trained in the use of such established mine rescue apparatus."

This Act also makes provisions for the filing of the plans of all abandoned coal mines.

Governmental inquiries and investigations

The Geology and Mines Act, 1907, provides for the Mines Branch of the Department of Mines. The functions of the Mines Branch are as follows:—

(a) to collect and publish full statistics of the mineral production and of the mining and metallurgical industries of Canada, and such data regarding the economic minerals of Canada as relate to the processes and activities connected with their utilization, and to collect and preserve all available records of mines and mining works in Canada;

(b) to make detailed investigations of mining camps and areas containing economic minerals or deposits of other economic substances, for the purpose of determining the mode of occurrence, and the extent and character of the ore-bodies and deposits of the economic minerals or other economic substances;

(c) to prepare and publish such maps, plans, sections, diagrams, drawings and illustrations as are necessary to elucidate the reports issued by the Mines Branch;

(d) to make such chemical, mechanical and metallurgical investigations as are found expedient to aid the mining and metallurgical industry of Canada;

(e) to collect and prepare for exhibition in the Museum specimens of the different ores and associated rocks and minerals of

Canada and such other materials as are necessary to afford an accurate exhibit of the mining and metallurgical resources and industries of Canada.

The following investigations, which relate to the conservation of minerals, have been made by the Mines Branch.

- (1) Electric smelting of iron ores.
- (2) Peat investigations.

The objects of the peat investigation were:—

First—To investigate the peat resources of Canada as to depth, quality and suitability of the individual peat bogs for fuel and other purposes.

Second—To demonstrate the process by actual operation.

Third—To demonstrate the economy effected in the production of power in gas producers adapted to the use of peat as fuel.

Fourth—To interest capital in the further development of the peat industry.

Fifth—To create a market for peat.

Preservation of Life

Owing to the fact that many fatalities have resulted from the use of explosives in mining and industrial work in Canada and as there has never been any legislation dealing with the inspection of explosives, the Mines Branch, Department of Mines, have framed an Explosives Bill which will be presented to Parliament this year. This Bill makes provision for the classification, authorization, storage, and transportation of explosives, and the issuance of licenses to explosives factories, and storage magazines; also for the establishment of a technical explosives division, comprising inspectors and staff of expert chemical examiners.

Substitution of Water-power for Coal

There are no deposits of coal of any importance in Ontario and for economic reasons all the coal used in that province is imported from the United States. The government, realizing the importance of obtaining a permanent supply of cheap power other than coal, formed a policy¹ by which the people of Ontario are assured of obtaining electric light and power, generated from water-power, at less cost than such could be supplied by large corporations controlling the sources of hydro-electric energy.

¹ This policy is fully discussed under "Water-Power."

In 1911, over 530,000 horse-power were developed from water-powers in Ontario. This is equivalent to an annual production of about 11,700,000 tons of coal.

The Commission of Conservation

The Conservation Act, 1909, established a Commission for the Conservation of Natural Resources. The Commission of Conservation is not an executive nor an administrative body but is constituted for the purpose of collecting exact information, deliberating upon, digesting and assimilating this information so as to render it of practical benefit to the country, and for the purpose of advising upon all questions of policy that may arise in reference to the actual administration of natural resources where the question of their effective conservation and economical use is concerned.

One of the several Committees into which the Commission is divided, is especially charged with the conservation of minerals.

The Commission of Conservation has investigated the coal mines of Alberta, Saskatchewan and British Columbia to ascertain the methods of mining employed at each mine, the size of rooms and pillars, methods of drawing pillars, depth of cover over the workings and its effect on the method of mining and extraction, percentage extraction of coal, the waste of unmarketable coal (slack) and the provisions made for safeguarding the lives of the workmen.

Waste

In the investigation it was found that there was in Saskatchewan, Alberta and British Columbia, a considerable waste of slack coal which had been mined and brought to the surface. This waste of unmarketable slack coal varies from 10 to 35 per cent. of the output. In Saskatchewan, 10 to 25 per cent. of the output from the mines is slack coal which is dumped on the ground and wasted. In the vicinity of Estevan 10 to 12 per cent. of the output from some of the larger mines is dumped on the prairie and burned. It is necessary to remove this coal (lignite) from the mine plant as it readily ignites by spontaneous combustion.

The waste of slack coal varies from 10 to 12 per cent. in the Lethbridge district, and from 20 to 35 per cent. in the Edmonton

district. In the Crow's Nest Pass district in Alberta and British Columbia, the coal is of better grade and some of the slack is marketable; the remainder is made into coke in beehive coke ovens. At Bankhead, briquettes are made from the slack coal. On Vancouver island, some of the large producing mines waste from 10 to 15 per cent. of their output of slack coal, and, unfortunately, it is generally dumped into the sea. The high freight rates make it impossible to market this slack at a profit.

As a result of this investigation it was advised:

(1) That in order to ascertain the price of coal in different parts of the West, and which portions of the country are supplied with coal from the different mining centres, also to determine to what extent the Canadian market is invaded by American coal, it is necessary that a study be made of the prices of coal in Canada and the freight rates on the same from the mines to the market.

(2) That, owing to the necessity of obtaining a suitable domestic fuel and cheap power for the Prairie provinces, it is recommended that investigations be carried on with the view to utilizing the lignites which underlie the greater portion of these provinces.

All the coke produced in Alberta and British Columbia is made in beehive coke ovens and the by-products—gas, tar and ammonia—wasted. The only redeeming feature in this practice is that the coke is made from what might otherwise be waste slack coal. On the other hand, if by-product coke ovens were used the tar obtained could be used as a binder in the manufacture of briquettes.

The following recommendations made by the Commission, in a report published in 1911, refer to certain advised legislative enactments which are necessary to prevent the waste of mineral resources, and to further safeguard human life:

(1) It is advised that the Dominion regulations, relating to the disposal of petroleum and natural gas rights in the provinces of Manitoba, Saskatchewan, Alberta and the Northwest Territories make provision for the plugging of all abandoned natural gas wells, and that a severe penalty be imposed for wilfully allowing gas to waste.

(2) Records of all drill holes (diamond, keystone, calyx, etc.) should be filed with the Government.

(3) The plans of the working of all abandoned mines should be filed with the Government.

(4) Owing to the high death rate in coal and metal mines, it is advised that a Royal Commission be appointed to investigate mine accidents in Canada.

THE STEPS WHICH HAVE BEEN TAKEN IN CANADA FOR THE PRESERVATION OF THE LIVES AND HEALTH OF EMPLOYEES IN MINING AND METALLURGICAL INDUSTRIES

The steps which have been taken in Canada for the preservation of the lives and health of employees in mines are in part prescribed by statute and in part are the result of voluntary effort among the mining companies concerned.

The following Provincial statutes contain provisions intended to safeguard the health and lives of employees in mines:

| | |
|-------------------|---|
| Nova Scotia: | Chap. 19—1900 (coal mining); |
| | Chap. 20—1900 (metalliferous mining); |
| | Chap. 13—1909; |
| | Chap. 37—1910; |
| Quebec: | Chap. 23—1911; |
| Ontario: | Chap. 21—1908; |
| | Chap. 17—1909; |
| | Chap. 10—1911; |
| Manitoba: | Chap. 113—R.S. 1902; |
| Saskatchewan: | Chap. 23—R.S. 1909 (coal mining); |
| Alberta: | Chap. 25—1906 (coal mining); |
| | Chap. 17—1908 (eight hour day in coal mines); |
| British Columbia: | Chap. 134—1897 (metalliferous mining); |
| | Chap. 35 —1909 (metalliferous mining); |
| | Chap. 33 —1911 (coal mining). |

It will be observed that some of the provincial statutes mentioned above deal with coal mining, others with metal mining. The coal mining areas of Canada are situated in British Columbia,

Alberta, Saskatchewan, and Nova Scotia, and are under regulations of the several Provinces which apply to this industry alone.

The Coal Mines Regulation Acts of these four Provinces, whilst differing in certain respects, all contain provisions designed to safeguard the lives and health of miners and others employed about the workings. These provisions relate generally to the following, amongst other subjects:

The employment of competent managers, overmen, shift bosses, firemen, shop lighters, and miners who must in all cases be possessed of prescribed certificates of competency;

The appointment of Government Inspectors to visit the mine workings to ensure compliance with the Provincial laws; to investigate accidents; and generally to safeguard the interests of those employed in the coal mining industry;

The regular inspection of the mines by the company's own officers, and the prompt investigation and reporting of all accidents;

The prohibition of female labour underground, and of boys under a specified age in and about the mines;

The keeping of plans above ground of all underground workings; The fencing of mine shafts and all abandoned places;

Provision for ventilation and an adequate supply of pure air underground;

The provision of means of ingress and egress by separate shafts; Provision that no mine employee shall remain underground for more than eight hours per day (in Alberta and British Columbia alone);

The provision of rescue stations in underground workings;

The withdrawal of workmen in case of the discovery of noxious gases or danger from other causes;

The use of safety lamps under certain conditions;

Timbering of underground workings;

Regulation of the use of explosives underground;

The provision of proper appliances for lowering and raising workmen in shafts;

The imposition of penalties for violations of the law, and of special penalties in cases of wilful neglect endangering life and limb;

The adoption of such further rules approved by the Provincial authorities as may appear best calculated for the prevention of accidents, and for the safety of persons employed in mines;

Properly constructed ambulances or stretchers, with splints and bandages, to be kept by mines for immediate use in case of accident (in Alberta alone);

The provision by mining companies of oxygen helmets or other mine rescue apparatus, so placed as to be available for immediate use (in British Columbia alone).

The Government of British Columbia has established mine rescue stations at Nanaimo, Cumberland, Middlesbro and Hosmer for the purpose of supplementing, in case of need, the colliery installation of mine rescue apparatus. The Government of British Columbia is also said to have under consideration the advisability of procuring a special car fitted up with a complete equipment of mine rescue apparatus so that in case of accident the same may be despatched to the scene of the accident with as little delay as possible.

The Province of Alberta has established a mine rescue station at Frank for the purpose of supplementing, in case of need, the colliery installations of similar apparatus, principally in the Crow's Nest Pass district.

Oxygen helmets have also been voluntarily, and at their own expense, provided by the Dominion Coal Company, operating large coal mining properties in the Province of Nova Scotia. Two main rescue stations have also been erected by the Dominion Coal Company, and steps have been taken to train men in the use of the rescue apparatus.

This system has also been established by the Nova Scotia Steel and Coal Company who are the next largest employers of labour in that Province.

The requirements of the Provincial statutes applicable to metalliferous mining include provision for the regular inspection of mines by the companies' own officers and by Government Inspectors; the prompt investigation and reporting of all accidents; the prohibition of female labour underground and of boys under a specified age in and about mines; the keeping of plans above ground of all underground workings; the fencing

of mine shafts and all abandoned places; provision for ventilation and for an adequate supply of pure air underground; the provision of means of ingress and egress by separate shafts; the timbering of underground workings; and the provision of safe apparatus for lowering and raising persons in mine shafts.

LIST OF FACTORIES, ACTS AND AMENDMENTS OF THE SEVERAL
PROVINCES

N.S.

- 1901 c.1
- 1909 c. 36.
- 1910 c. 17 sec. 20.

Quebec

- R. S. Sec. 3019
- 1890 c. 26; 1894 c. 30; 1894 c. 31; 1910, c. 27.

Ontario

- R. S. O. c. 256; 1901 c. 35; 1902 c. 36; 1903 c. 7, s. 46;
- 1904 c. 26; 1905 c. 13, s. 30; 1908 c. 57; 1910 c. 17, s. 5.

Manitoba

- R. S. 1902 c. 62; 1904 c. 16.

Saskatchewan

- R. S. 1909 c. 17; 1910-11 c. 41, s. 6.

British Columbia

- 1908 c. 15; 1910 c. 18.

(Short abstracts of the documents, in the Spanish language, obtained through His Excellency the Chilean minister, Washington, D. C.)

REGULATIONS ESTABLISHED BY THE GOVERNMENT
OF CHILE IN ORDER TO PROMOTE THE PRACTICAL
CONSERVATION OF THE NATURAL RESOURCES
OFFERED BY THE WATERS (OF THE COUNTRY),
TO OBTAIN MAXIMUM WATER POWER IN
ORDER TO SECURE TO THE COMMUNITY
AND TO THE STATE THE MAXIMUM
OF ADVANTAGES. CERTAIN FACTS
ILLUSTRATING THESE PROVISIONS

The idea of making an orderly and methodical study of the great hydraulic powers which exist in the waters that descend from the Cordillera of the Andes originated in the National Society of Mining, in view of the great application, importance and value which in general throughout the world the hydraulic water powers have obtained.

In consequence, the National Society of Mining petitioned the Government to create an official office which should be charged especially with the above named studies, under date of July 14, 1909. Then follows the text of the petition of the Society of Mining. This petition recites what has been done in the Alps in Italy, Switzerland and France in the matter of studying and measuring water powers—pages 2 to 4. There appears to be no reference to the studies in the United States. Continuing, the petition of the Society of Mining quotes from Blondel of Paris a statement of the importance of electricity in modern industry—pages 4 and 5. The petition then discusses the natural conditions which make Chile particularly a region for the development of electrical power from water power. It says in effect:—

“Again the natural conditions of our country, which are so exceedingly favorable in view of the numerous and great waterfalls, make it evident that it would be of the greatest interest to have at hand the technical knowledge essential to their use, in

order that we may be prepared at the time when the opportunity presents itself. It has been shown that studies of hydraulic power require to be extended over a term of ten years, more or less, even in such a country as Switzerland. In our country (Chile), we would have to consider at least double that time (this clearly refers to the measurement of stream flow and to the fact that, as yet, there are no adequate records for the Chilean streams). Yet, continues the petition, the problems of electrification of our railways, urban lines, the lighting of cities, and use of motive power, together with the problems of electrical chemistry and metallurgy, demand that we should prepare ourselves in the near future."

On page 6, the memorial gives the following illustration:

"To illustrate by example the importance which all such studies will have, it would suffice to say that the state railways alone have consumed during the past year in the neighborhood of 400,000 tons of coal, representing a value of more than \$14,000,-000 pesos. One peso (Chilean) is 21 cents. This sum could be annually economized by the electrification of the railways and would correspond to an invested capital of 140,000,000 pesos. In view of these considerations, the National Society of Mining deems it expedient to petition the administration to create an office under the Minister of Industries to organize the work necessary to the study of our water powers."

The memorial then suggests that this service should consist of one chief engineer, two assistant engineers, two levelmen, one chief clerk and two draftsmen.

In consequence of this petition, the Government, on the 26th of July, 1909, issued a decree which created a "Section of Studies of Water Powers of the Country." This decree is given in full—pages 7 and 8, and runs:—

SANTIAGO, July 26, 1909.

Considering that it is of public interest to know all of the necessary data in order to be able to use the great water powers of the country, which are capable of being employed in the electrification of railways, in lighting, motive power, and urban traction, as well as in agriculture, manufacturing, chemical and metallurgical industries, it is decreed:

1. That the engineer, Oscar E. Schmidt, shall be employed under the direction of the Commission which is designated in article 5 of this decree, to organize and direct the service of the studies of the usable water powers, and especially those which are situated within the mountainous regions of our national territory, as they are those whose development is the most facile and economical.

2. In order to carry out these studies, the engineer Schmidt will take as a plan of his work, at least in its general lines, that of the analogous operations executed by the Hydrometric Section of the Swiss Federal Government, and also those of the French Commission, designated by the Minister of Agriculture of France under date of March 25, 1903.

3. Senor Schmidt will present a definite plan which he will thereafter follow to carry out the indicated studies, keeping in mind that his initial object is to make known those great powers which are found to be most favorably situated for use under economic conditions, without, however, interfering with the development of the complete statistics of the available forces.

4. Senor Schmidt will begin the above mentioned studies in the central portion of the country, where the water powers may find the largest and most immediate application.

5. Senor Schmidt will be directed in the exercise of his duties by a Commission of Directors composed of three members chosen one each from the National Societies of Mining, for the Promotion of Manufacturing, and of Agriculture. The President, who chooses this Committee, will be the medium of communication with the Minister of Industries and Public Works.

One may observe that the activity of the Government in the study and use of the natural water powers dates from the time of this decree. Previously the Government had left such activities to private enterprise, limiting itself to concessions of water for industrial purposes under easy conditions and with liberality. The object of the Commission of Directors was to bring the Government studies into close touch with the actual conditions of the various industries which might be interested.

(The names of the members are then given—page 9.)

With the presentation of definite projects for the electrification

of the Transandean Railway via Juncal, and of a portion of the Great Central State Railway south from Santiago, as also of the principal line of the State Railway between Santiago and Valparaiso, and the branch to Los Andes, the Government began to occupy itself more closely with the study and computation of the hydraulic powers of the country.

The Section of Study of Water Powers began this work at the close of 1909 under very moderate conditions, seconded in its work by the National Societies of Mining and Manufacturing. In view of the projects for the electrification of the railways between Santiago and Valparaiso—187 kilometers long—and the branch from Las Vegas to Los Andes—45 kilometers long—the first investigations were directed to the hydrographic study of the River Aconcagua and its tributary, the River Maipo. The catchment basins which were subsequently systematically studied were those of the Cachapoal and Bio Bio. These are all in the central region of the country where there is the largest population and where most of the industries of the republic are situated.

The memorial, on page 10, then recites further operations of the Section, including the periodical measurements of water in various important sections of the rivers Aconcagua and Maipo already referred to, and for further information on these points refers to a pamphlet "Organizacion de la Seccion y Reg lamen tacion jeneral de sus traba jos y servicios," which is among those submitted.

It may be observed that the organization of the Section is not only in a certain sense scientific, but is especially designed to be practical.

The memorial then goes on to point out at some length that the studies of water powers comprise three distinct lines of expert work—one section being charged with investigations designated as scientific, another having to do with the measurement of water powers, and a third with their application and utilization. (It is not clear just what distinction is made by "scientific" in this case.)

Pages 12 to 15 recite various water powers distributed throughout central Chile, indicating in a general way their character, distribution of the water-falls, amount of power, etc.

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